

M. N. KHRAMKINA
**LABORATORY
MANUAL
OF ORGANIC
SYNTHESIS**



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ПО ОРГАНИЧЕСКОМУ
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M. N. KHRAMKINA
**LABORATORY
MANUAL
OF ORGANIC
SYNTHESIS**

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PREFACE

In conformity with the curriculum, this practical course in organic synthesis for technical school students gives the principal methods of organic synthesis used in factories and laboratories and enables students to acquire skills for working in enterprise laboratories and research centres.

When carrying out operations in organic synthesis, technical school students should become practically acquainted with the main chemical reactions and learn how to perform experiments.

This book explains the modern theoretical concepts of organic chemistry to the extent needed for carrying out synthesis. A more detailed exposition of theoretical aspects, especially those involving the reaction mechanisms, is given in textbooks of organic chemistry.

This textbook presents a large number of syntheses. The greatest attention is devoted to laboratory operations which are of practical and methodological importance. If need be, a laboratory operation in a given subject can be replaced by a similar one in the students' future speciality. In addition, when there is a large number of syntheses, the instructor can select those needed for review problems to see how well the students have learned their material.

Certain guides to organic synthesis were used when the textbook was being written.

This edition of the textbook has new material on the mechanism of individual reactions and a chapter on the identification of organic compounds.

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Part I

METHODS USED IN ORGANIC SYNTHESIS

Chapter 1

WORK AND SAFETY RULES

When commencing work in organic synthesis, it is especially necessary to have a good understanding of the rules and safety regulations of doing work in an organic synthesis laboratory as well as precautions against accidents, and to bear in mind that disorder, haste and carelessness can spoil work and even cause accidents.

1.1. SAFETY RULES IN THE ORGANIC SYNTHESIS LABORATORY

1. When working in a chemical laboratory, there should be silence, order and cleanliness; work should be done rationally, accurately, carefully and quickly, but without haste.

2. Do not commence work without the instructor's or the laboratory technician's permission.

3. Never work alone in the laboratory.

4. Every student should work at the place which is either given to him or specially used for a certain operation.

5. The bench should be kept clean and uncluttered.

6. Save gas, water, electricity and reagents.

7. Wear a laboratory coat while working; have some soap and a towel in the laboratory.

8. Handle chemical laboratory equipment, reagents and apparatus with care. To preclude accidents caused by splashing droplets of the reaction mixture, do not look into the test tube or the flask from above.

9. Do not work with dirty vessels, and do not leave them unwashed.

10. Do not use any apparatus without checking it first. An apparatus being used must not be left unattended.

11. Do not take apparatus, vessels and reagents out of the laboratory.

12. Work with poisonous substances in a fume cupboard.

13. Take precautions when working with explosives and highly flammable substances.

14. Do not pour the residues of acids, alkalies, flammable liquids, and so forth, into the sink. Pour them into special flasks placed in the fume cupboard. Do not throw paper, sand and other solids into the sink.

15. Neutralize the solutions containing concentrated acids and alkalies before pouring them down the drain. Acrid and poisonous substances should be made harmless by chemical treatment or be burned at a special place outside the laboratory, preferably somewhere outdoors.

16. Do not leave any substances in vessels without labels.

17. Work with acids and alkalies only on benches having a special covering.

18. Do not mistake the stoppers of flasks containing different reagents so as not to contaminate the latter.

19. When weighing dry reagents, do not pour them directly in the balance pan.

20. Never smoke and eat in the laboratory.

21. In case of fire, immediately switch off all the gas in the laboratory, remove all flammable substances from the premises, pour sand on the source of the fire or cover it with a blanket and report the fire to the fireman on duty. Learn and obey the fire prevention rules.

22. When leaving the laboratory, make sure the gas, water and electricity are switched off.

1.2. PRECAUTIONS AND FIRST AID IN CASE OF ACCIDENTS

When working in the organic synthesis laboratory, it is necessary to take every precaution; the slightest carelessness can lead to serious consequences.

WORK WITH POISONS AND CAUSTICS

Most chemical compounds are more or less toxic. Therefore, anyone who is beginning synthesis *should have good knowledge of the toxic properties* of the substances with which he is working and, if need be, should be able to help in an emergency.

When working with poisons and caustics, the following rules should be obeyed:

1. A premise should have gas masks, safety face screens, and goggles.

2. Work with especially dangerous substances (*bromine, concentrated acids*, etc.) should be carried out under the instructor's or the laboratory technician's close supervision.

3. All the operations involving poisonous and flammable gases and vapours should be carried out in the fume cupboard.

When working in the fume cupboard:

(a) do not close the doors tightly, but leave them on the level indicated by the instructor;

(b) do not put your head into it;

(c) do not dismantle an apparatus until a poisonous gas or vapours are removed from it by water or air under a hood;

(d) a gas mask should be at hand when working with *chlorine, bromine* and other poisonous substances.

4. *Caustic alkalies, soda lime, iodine, bichromate, and aniline salts* should be ground in a fume cupboard, in the course of which a safety face screen or goggles should be worn.

5. When working with *concentrated acids, oleum and ammonia*, the following precautions should be taken:

(a) pour the given liquids only through a funnel and under a hood;

(b) when diluting concentrated sulphuric acid, pour the acid in portions into water and stir slightly;

(c) do not dilute oleum with water;

(d) only thin-walled chemical laboratory equipment can be used when concentrated sulphuric acid is being diluted in water, when a chromic acid mixture is being prepared, and when concentrated sulphuric and nitric acids are being mixed.

6. Do not pour hot liquids into thick-walled vessels and apparatus.

7. Work involving bromine should be done in a fume cupboard; in this case, the following precautions should be taken:

(a) do not inhale its vapours, and protect the eyes and hands;

(b) when bromine is being poured, carefully remove the drop from the edge of the flask neck by putting it against the edge of the vessel;

(c) wear rubber gloves when pouring large quantities of bromine.

8. Care should especially be taken when working with *metallic sodium*:

(a) to protect the face and the head, goggles and screens of plastic glass should be used;

(b) sodium should be kept under a kerosene layer in a cylinder closed with a cork stopper;

(c) sodium should be cut only on *dry* paper;

(d) the cut-off pieces of sodium should not be thrown into the sink or be kept bare on the bench, but should immediately be collected in a cylinder containing kerosene;

(e) pick up sodium only with pincers or forceps;

(f) halogen derivatives of the fatty series should not be dried with sodium if they are not in a solution;

(g) sodium should not be brought into contact with water and carbon tetrachloride;

(h) small remnants of unreacted sodium should be destroyed by adding small portions of butyl or amyl alcohol;

(i) reactions with metallic sodium should be carried out, not in a boiling water bath, but in a sand or oil bath.

WORK WITH HIGHLY FLAMMABLE SUBSTANCES AND EXPLOSIVES

In preparative organic chemistry, *flammable* solvents, such as *ethers*, *alcohols*, *benzene* and *acetone*, are used often. Care should especially be taken when working with these substances, because their vapours are highly flammable.

The following must be borne in mind:

1. Do not keep these solvents near a flame, in a warm place or near heaters.

2. Do not heat them on an open flame, on a net, near a flame or in open containers, but only in a water bath with a reflux water condenser.

3. Do not keep them in a thin-walled, tightly stoppered vessel.

4. Do not pour them into the sink.

5. Do not keep large quantities of them on the workbench.

6. Distil them only in a water bath using a water condenser on a special laboratory bench. When working with ether, the water bath should be heated at a distance from the place of distillation.

7. Do not distil ether which has been stored for a long time without checking whether peroxides are present.

8. If, for some reason, a large amount of a highly flammable liquid has been spilled in the laboratory, it is necessary to turn off all the burners and electric heaters, open the windows and collect the spilled liquid with a piece of cloth or a towel.

RULES OF HANDLING GLASSWARE

1. When breaking glass tubes or rods that have been notched with a file, try to pull the tube apart, as it were, so as not to cut the hands against the glass edges.

2. When inserting a glass tube, a condenser, a dropping funnel and a thermometer into a stopper, it is necessary to hold them

with the hand as close as possible to the end being inserted. They should be slightly twisted, and not pressed, to the stopper. If rubber stoppers are used, they should be lubricated with glycerol, and then excess glycerol should be removed.

3. Do not heat thick-walled equipment.

4. Be careful when working with glassblowers, and take care of the eyes.

FIRST AID IN CASE OF BURNS, POISONINGS AND OTHER ACCIDENTS

1. In case of minor *heat burns*, the skin should be washed with alcohol and then treated with glycerol or Vaseline. When a burn is more severe, it should be treated with an approved burn ointment (such as the sulphonamide emulsion) after being washed with a concentrated solution of potassium permanganate and alcohol.

2. In case of *bromine burns*, thoroughly wash the affected place first with benzene or alcohol, and then with a 10 per cent sodium thiosulphate solution. After inhaling bromine vapours, smell a dilute ammonia solution and go out into the open.

3. In case of *burns by liquid phenol*, rub a little glycerol into the whitened region of the skin until the colour normalizes, and then wash the affected area with water and apply a cotton or gauze dressing wetted with glycerol.

4. In case of *burns by strong acids*, flood the affected parts immediately and thoroughly with much water and then with a 3 per cent soda or ammonium hydroxide solution.

5. In case of *burns by strong alkalies*, the skin should be washed with water and then neutralized by a 1 per cent boric acid solution. Ammonia scarcely affects the skin, but if it gets in the eyes, it can greatly injure them and even cause blindness.

6. If reagents accidentally get into the organism, it is recommended to drink much water. In addition, drink: (a) a glass of 2 per cent sodium bicarbonate in case of poisoning by acids and (b) a glass of 2 per cent acetic or citric acid in case of poisoning by alkalies.

7. In case of poisoning, take the victim into the open, perform artificial respiration and call a doctor.

8. A person can cut and injure himself when he carelessly bends tubes or inserts a tube or a thermometer into the neck of a flask. In case of cuts, it is necessary above all to remove bits of glass from the wound, disinfect its edges by a 3 per cent alcoholic solution of iodine, and then cover it with a sterile bandage. In case of heavy bleeding, apply an elastic bandage above the wound and call a doctor or send the victim to a hospital (poly-clinic).

EXTINGUISHING LOCAL FIRES AND BURNING CLOTHES

1. If a flammable liquid bursts into flame, turn off all the burners, cover the flame with an asbestos square or sand, or use a carbon dioxide extinguisher.

2. Water-soluble flammable substances, such as alcohol and acetone, can be extinguished with water.

3. If a water-insoluble substance (e.g., ether, benzene, gasoline, turpentine) is burning, water cannot be used for extinguishing the fire because, instead of dying out, the fire can even intensify. In this case, the fire should be extinguished with sand or a fire extinguisher.

4. If a person's clothes catch fire, do not let him run; cover him with a laboratory coat, a jacket, a tarpaulin, or a woollen or felt blanket, which should always be kept in a visible place within easy reach.

1.3. PRINCIPAL LABORATORY EQUIPMENT

When preparing for synthesis, it is important to select the appropriate equipment and assemble the necessary apparatus. This should be done especially carefully; otherwise, part of a substance

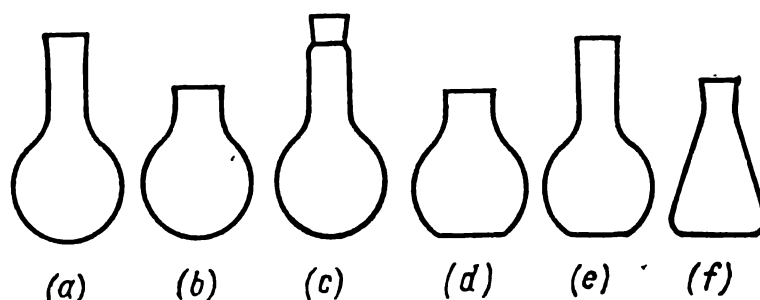


Fig. 1.1. Flasks:

a—narrow-mouth round-bottom; *b*—wide-mouth round-bottom; *c*—with a ground-glass joint; *d*—wide-mouth flat-bottom; *e*—narrow-mouth flat-bottom; *f*—conical

can be lost, and there can be a fire or an explosion. Before assembling an apparatus, it is necessary to prepare for a given operation, i.e., it is necessary to know the theoretical material relating to a given synthesis, how work should be done, and the course of the operations which must be carried out as well as safety rules.

Flasks and beakers are the principal laboratory equipment; borosilicate glass is the material most commonly used for making them. Syntheses are carried out mostly in flasks, which differ in their capacity and shape. When a reaction is proceeding while heating the reaction mixture to the boiling point, round-bottom flasks should be used because they are unaffected by jumps which originate when a liquid boils. They can be wide- and narrow-

mouth, and with or without ground-glass joints (Fig. 1.1). Round-bottom flasks are used for syntheses, for distillation under atmospheric pressure and with water vapour, and as receivers in vacuum distillation.

Special round-bottom flasks, such as the Anschütz and Würtz flasks (Fig. 1.2), the Claisen and Favorsky flasks and two- or

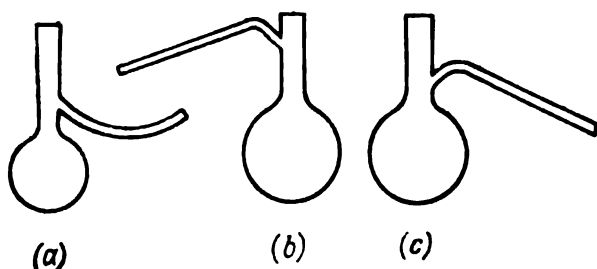


Fig. 1.2. Distilling flasks:
a—Anschütz flask; b, c—Würtz flasks

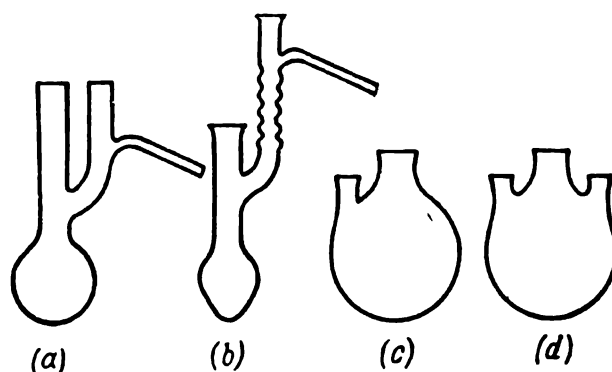


Fig. 1.3. Special round-bottom flasks:
a—Claisen flask; b—Favorsky flask; c—two-necked flask; d—three-necked flask

three-necked flasks (Fig. 1.3) are used for distilling liquids. The Anschütz flasks are used for distilling rapidly solidifying substances, while the Claisen flasks are used in vacuum distillation. Two- or three-necked flasks are very convenient for carrying out several operations simultaneously, e.g., in the case of heating with a reflux condenser, the reaction mixture must be uniformly mixed

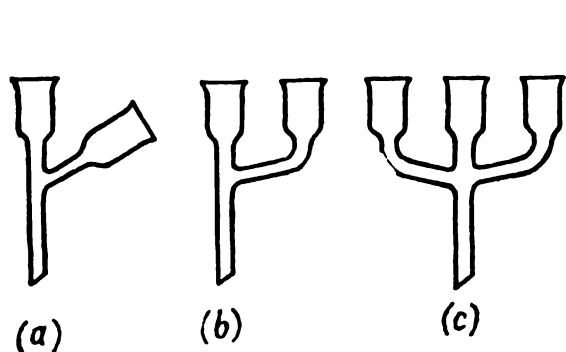


Fig. 1.4. Adapters:
a, b—two-mouth; c—three-mouth

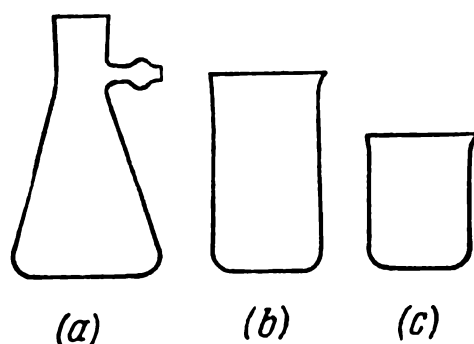


Fig. 1.5. Bunsen flask (a) and beakers (b, c)

and the components must be introduced slowly through the dropping funnel. If the laboratory does not have such flasks, round-bottom flasks with adapters (Fig. 1.4) are used.

Flat-bottom flasks, both narrow- and wide-mouth ones (see Fig. 1.1d, e), are not used for vacuum operations, because they burst under external pressure. They are also not used for high-temperature operations. They should be used for preparing reagents and carrying out reactions at temperatures below 100°C, when it is not necessary to isolate a process from moisture and air.

They should be used also as receivers in distillation with steam or under atmospheric pressure.

Conical (or Erlenmeyer) flasks (see Fig. 1.1f) are used for crystallization, preparing reagents, as receivers, and for simple operations, when there is no need to protect a process from moisture and air, as well as for several other purposes.

Bunsen flasks (Fig. 1.5a) are used for vacuum suction and, less frequently, as receivers in vacuum distillation. They are of different capacities and shapes; in most cases, conical flasks are used because they are the most stable. Bunsen flasks are made of thick glass because otherwise they could be crushed by atmospheric

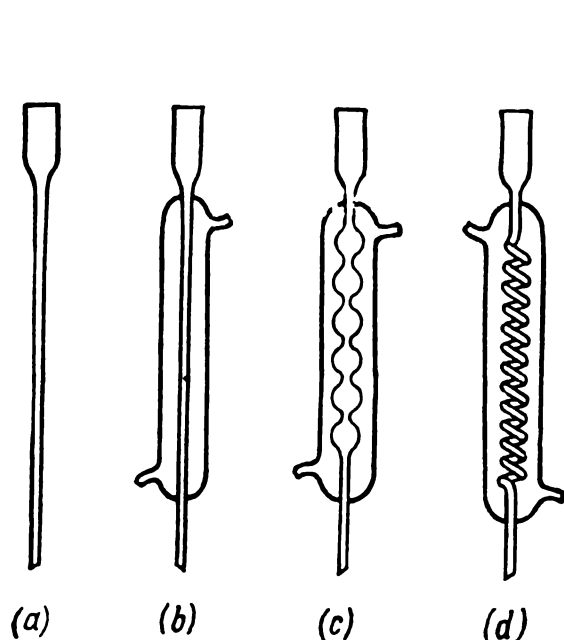


Fig. 1.6. Condensers:
a—air; b—Liebig; c—Allihn; d—coil

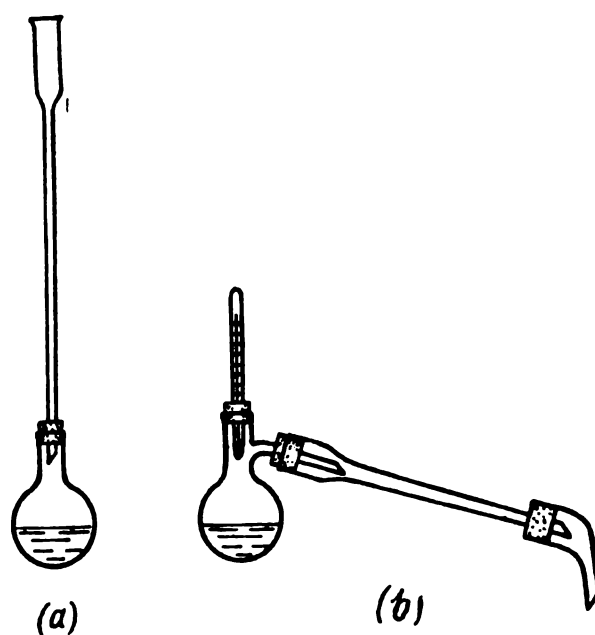


Fig. 1.7. Use of the air condenser,
both reflux (a) and downflow (b)

pressure. Before commencing work, new Bunsen flasks are washed and kept under vacuum for 15 minutes. When carrying out tests and working with Bunsen flasks, they should be wrapped in a towel or put in a metallic net.

Beakers (Fig. 1.5b, c) are employed for carrying out reactions below 100°C. Their main purpose is to be used as auxiliary vessels. Beakers cannot be used for operations involving low-boiling and flammable solvents, because these liquids are volatile.

Condensers (Fig. 1.6) are used for cooling and condensing vapours in reactions with organic compounds. They are called reflux condensers when the vapours being condensed in them return to the reaction mixture (Fig. 1.7a), and downflow condensers when, in distillation, the condensate from the condenser enters the receiver (Fig. 1.7b). There are two coolants for condensers: air (air condenser) and water (water condenser).

The simplest condenser is the air condenser, which can be used as both a reflux condenser and a downflow condenser even for liquids with a boiling point of 150°C or higher; water condensers are not used for such liquids, because the condenser tube can burst as a result of a sharp change in temperature.*

The Liebig condenser is commonly used in the laboratory; it is employed as a downflow and a reflux condenser. It consists of an external jacket, which is secured to the inner tube or is connected to it by rubber tube sections. The external jacket has two side arms. Rubber tubes are put on them, and one tube is connected to the water faucet, while the other leads into the sink. In this case, the following rule should be borne in mind: if the Liebig

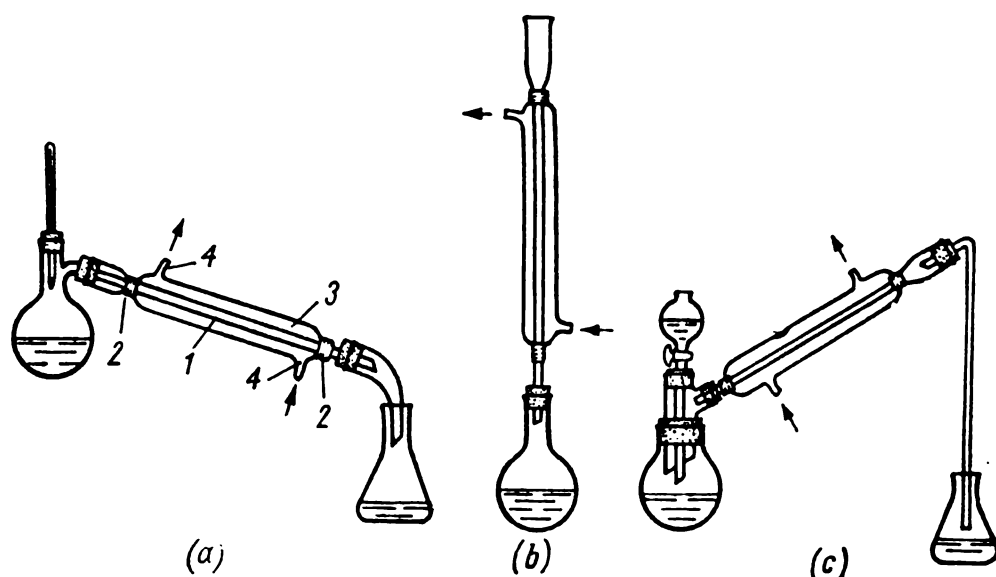


Fig. 1.8. Use of the Liebig condenser, both downflow (a) and reflux (b, c):
1—inner tube; 2—connecting rubber tubes; 3—external jacket; 4—side arms

condenser is used as a downflow condenser, water is supplied according to the counterflow principle, i.e., water should move toward the vapours of the liquid being cooled (Fig. 1.8a). But if the condenser is used as a reflux condenser, the counterflow principle is not observed and water is supplied to the lower side arm so as to completely fill the condenser with water and effectively condense the vapours of the reaction liquid (Fig. 1.8b, c).

In laboratories, other types of condensers, the Allihn and coil condensers, are used in many cases. The Allihn condenser (see Fig. 1.6c) is used in most cases as a reflux condenser, because the bulb expansions in the inner tube substantially improve its cooling action. The coil condenser (see Fig. 1.6d) is always used only as a downflow condenser for low-boiling substances. It is never used

* For liquids with a boiling point of $140\text{--}160^{\circ}\text{C}$, use can also be made of the water condenser, but without water circulation.

as a reflux condenser, because the condensate, which runs off poorly along the bends, can splash out of the condenser.

Condensers can operate normally only when water pressure is constant, and therefore it should always be seen that the flow of cooling water must be steady; otherwise, there can be an accident.

Dropping funnels (Fig. 1.9) are used for adding liquids slowly to the reaction mixture. Before commencing work with the dropping funnel, the ground-glass joint of the stopcock should be slightly lubricated with Vaseline; the stopcock can then be easily opened, which is very important because when the stopcock is difficult to turn, it can be broken or the entire apparatus can be

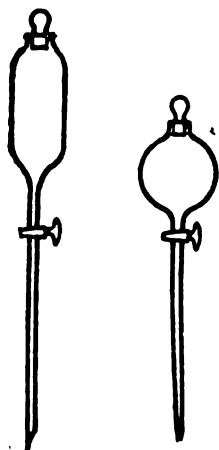


Fig. 1.9. Dropping funnels

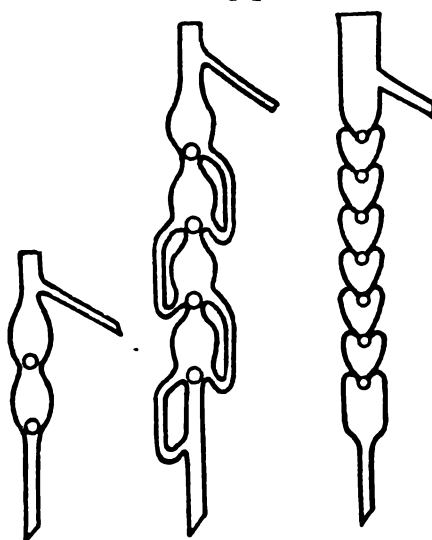


Fig. 1.10. Dephlegmators or fractionating columns

damaged while opening it. After lubricating the stopcock, it is necessary to check whether the funnel is absolutely leakproof (when the stopcock is closed).

Dephlegmators or fractionating columns of different designs (Fig. 1.10) are often used in fractional distillation (see p. 77). Their lower end is inserted into a stopper which is fixed in a flask neck, and a thermometer is put into the upper opening, while the discharge tube of the dephlegmator is connected to the condenser (Fig. 1.11).

The **bent adapter** is used for drawing off the distillate during distillation. It is fitted to the condenser by means of a stopper.

Calcium chloride tubes (Fig. 1.12) are used when reagents must be protected from the action of moisture. The calcium chloride tube contains a layer of calcium chloride as grains; 1-1.5 cm from the top of the tube remains empty, while a small layer of cotton is put on the top and the bottom.

Porcelain ware is more durable than glassware, and it can be strongly heated. But porcelain articles also have disadvantages:

they are heavy, nontransparent and considerably more expensive than glass articles. Porcelain is used to make beakers (Fig. 1.13a), evaporating dishes (Fig. 1.13b), mortars and pestles (Fig. 1.13c),

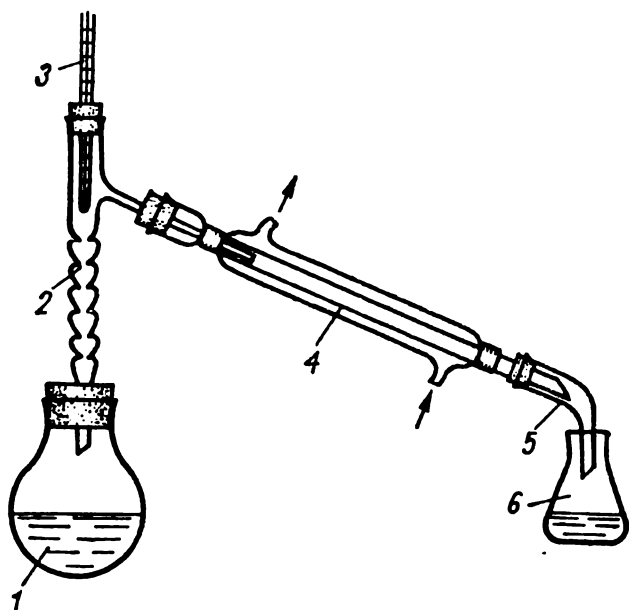


Fig. 1.11. Fractional distillation apparatus:

1—reaction flask; 2—dephlegmator; 3—thermometer; 4—condenser; 5—bent adapter; 6—receiver

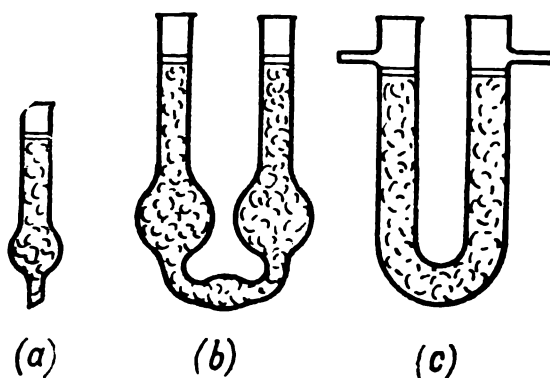


Fig. 1.12. Calcium chloride tubes:

a—simple; b, c—U-shaped

crucibles (Fig. 1.13d), Büchner funnels (Fig. 1.13e), spoons and spatulas, combustion boats, tubes, etc.

Stoppers (cork and rubber) are used for connecting glass parts of apparatus and tightly plugging up vessels. Ordinary cork

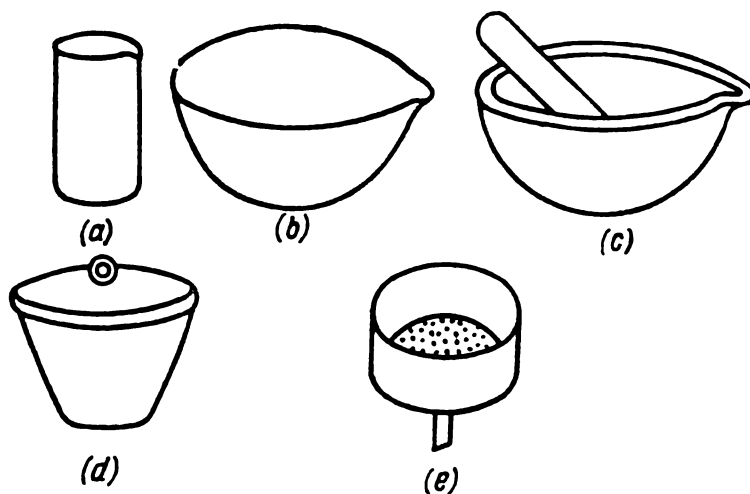


Fig. 1.13. Porcelain ware:

a—beaker; b—evaporating dish; c—mortar with a pestle; d—crucible; e—Büchner funnel

stoppers of good quality make a vessel or a device sufficiently airtight, but it should be borne in mind that cork stoppers which have been used are already contaminated, and they cannot be washed well owing to their porosity. A cork is so selected that its diameter is slightly greater than that of the opening to be plugged

up, and it should enter the opening with a slight effort. To make a cork stopper elastic and somewhat reduce its diameter, it should be squeezed with a special cork press (Fig. 1.14a). When a suitable stopper cannot be found, a large stopper should be fitted by using a knife or a file, or both.

Holes in stoppers are made by hand-operated borers (Fig. 1.14c) or mechanical borers, which should always be well sharpened by a special sharpener (Fig. 1.14b). The inner diameter of the selected cork borer should be slightly smaller than that of the tube to be inserted into the stopper. Before a rubber stopper is bored, it should be slightly heated in a water bath in a 2-3 per cent alkaline solution, and then washed with water and wiped, while the bore should be lubricated with Vaseline or washed with glycerol in order to reduce friction.

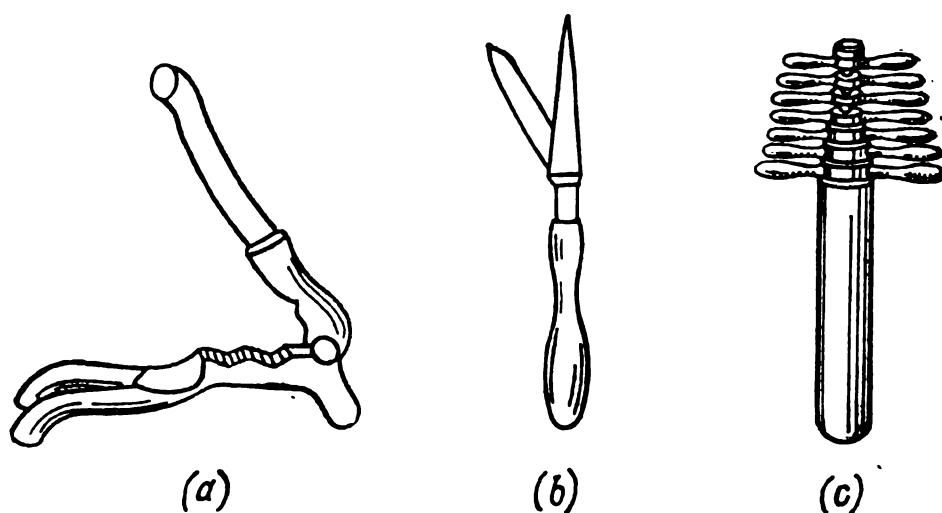


Fig. 1.14. Cork press (a), cork sharpener (b) and set of borers (c)

A stopper should be bored without haste and always at first from its narrow base, since this part will be in the vessel and should be even. In boring, the stopper is held in the left hand, while the borer, in the right; the borer is so held that its axis coincides with that of the stopper, while the hole made in the stopper should be parallel to the side of the vessel neck, as this will make it much easier to correctly assemble the vessel. Boring should be started by pressing on the stopper and slowly twisting the borer; one should not press hard on the borer, because then the holes in the cork stoppers become irregular and their edges ragged, and the holes in the rubber stoppers become much smaller in diameter.

It is more convenient to bore rubber stoppers by a special stopper boring machine (Fig. 1.15). By using it, uniformly bored holes can be obtained, which is not always possible with the hand-operated borer. After making a hole in the stopper, the borer is removed and the plugs left in it are pushed out with a metal rod

which is found in every set of borers. If the hole bored in a cork stopper turns out to be too narrow, it can be reamed with a round file. When working, it is often necessary to connect the flask to several devices (a condenser, a dropping funnel, a thermometer, etc.); a wide-mouth flask is then used and several holes are made in the stopper, or adapters are used (Fig. 1.16).

To make the stoppers very resistant to the action of corrosive vapours or gases (alkalies, acids, oxides of nitrogen, bromine and chlorine, etc.), they must be specially treated. Cork stoppers are heated for 15-20 min at 50°C in a solution consisting of three parts gelatin, five parts glycerol and 100 parts water. While continuously turning them with a glass rod, the stoppers are then

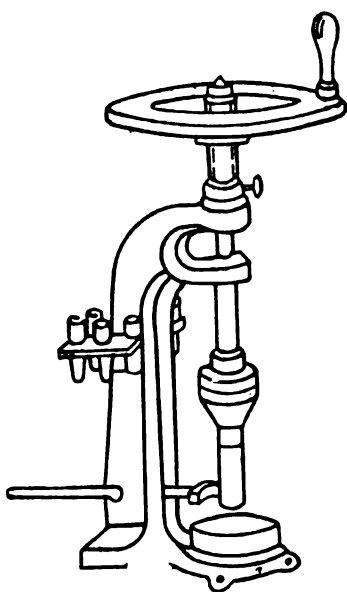


Fig. 1.15. Stopper boring machine

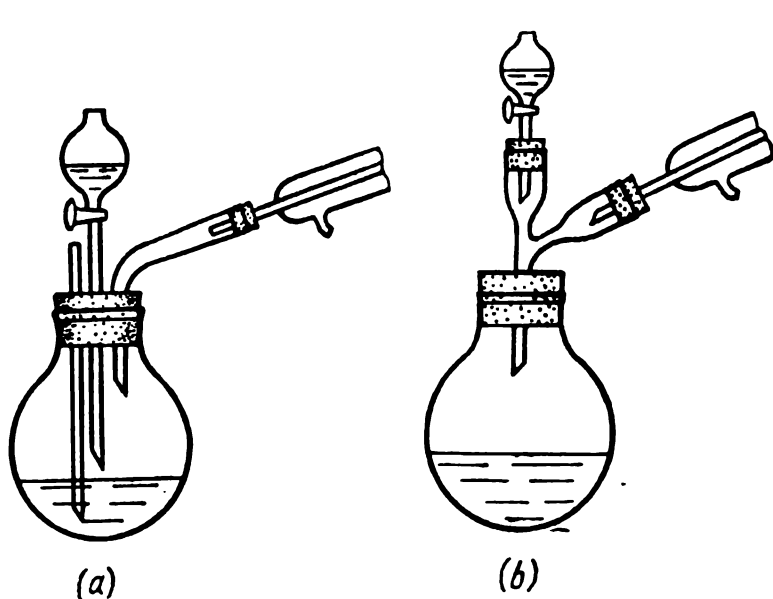


Fig. 1.16. Attachment of the reaction flask to apparatus:

a—by boring several holes in the stopper; *b*—by means of an adapter

dried and impregnated with a molten mixture consisting of 12 parts Vaseline and 42 parts paraffin. Afterwards, the cork stoppers are taken out and dried.

If rubber stoppers are used for a long time, they harden, crack and become unfit for reuse. Therefore, old rubber stoppers are put in paraffin heated up to 100°C , where they are kept for not more than one minute. To renew old cork stoppers, hot water is poured over them, and then they are put in a mixture consisting of 15 parts water and one part salicylic acid. Afterwards, they are washed with water and dried in the open.

It should be borne in mind that cork and rubber stoppers are very poorly resistant to high temperatures and many chemical reagents. Rubber stoppers poorly withstand temperatures above 140°C ; they swell and are destroyed easily under the action of benzene, toluene, ether, acetone, halogen derivatives and other substances, thus contaminating the reaction products. Cork stop-

pers are poorly resistant to strong acids and alkalies, and, owing to their porosity, cannot be used under vacuum.

Glass tubing of different diameters are used for connecting separate parts of an apparatus. To cut a piece of narrow glass tubing, a scratch is made on its surface with a file or a knife for cutting glass; then the tubing is held with both hands and the thumbs are met on the rear side just opposite the scratch. While pressing slowly outward with the thumbs, pull the tubing apart forcibly. Wide and thick tubes are not to be broken; to cut them, a cross-sectional scratch is made on them with a knife and a red-hot glass rod or wire is applied to the scratch; the tube then

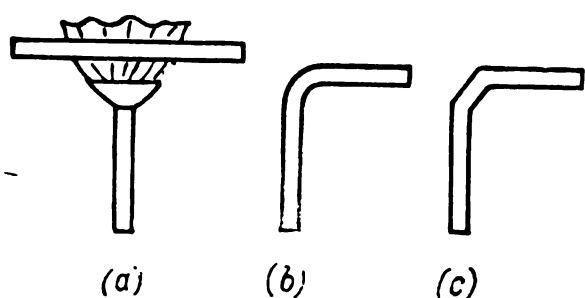


Fig. 1.17. Bending of glass tubes:

a—heating by a burner with the wing top;
b—a good bend; c—a bad bend

breaks, forming a uniform section. The cut-off ends of the tubes must be fire-polished. This is usually done in a burner flame. Fire polishing precludes hand injuries, allows the tubing to be easily put on the stopper, and prevents glass vessels from being scratched.

Glass tubings must be perfectly dry and clean when they are being treated in the burner flame.

Both heating and cooling should be performed gradually, because glass easily cracks when temperature changes suddenly. Fire polish the tubing by rotating it in a smoky and then in a high clean burner flame. After heating, the red-hot tubing is slightly cooled in a smoky burner flame and then allowed to cool on a piece of asbestos.

To bend glass tubings, it is necessary to have a special attachment for the burner, such as the *wing top* (Fig. 1.17), which produces a broad flat flame. The tubing, one end of which is closed, for instance, with a piece of asbestos, is uniformly and intensely heated in an area 5-8 cm long while being held by the cold ends and slowly rotated in the burner flame. As soon as the tubing becomes soft enough to begin bending under its own weight, it is taken out of the flame and bent very smoothly, raising the ends upwards and slightly blowing air into it. The bent place should then be heated in a smoky burner flame and allowed to cool slowly.

Capillary tubes are used very frequently in the laboratory. They are of two types. Some of them are used for determining the melting point of organic substances, while others, in heating and distilling liquids to both preclude overheating and create conditions for uniform heating.

To obtain capillaries of the first type, glass tubing is heated while continuously being rotated in a broad flat flame. When the tubing softens and begins to narrow down in the heated place, it

is taken out of the flame and pulled apart, though not very rapidly, while continuously rotated. As soon as it cools, it is cut into pieces about 4-5 cm long, the thin end is sealed, and the capillary tubes are used for determining the melting point.

Capillary tubes of the second type are made similarly, the only difference being that the softened tube is pulled apart rapidly. Their length depends on the size of the flask being heated. One end of the capillary tube is also sealed.

Capillary tubes for vacuum distillation are special ones. Both of their ends are open.

1.4. ASSEMBLY

Before pouring a liquid into a flask or filling it with some other substance, an apparatus must be assembled, while synthesis should be commenced only after checking that it is assembled correctly. Its separate parts should be connected carefully so as not to break them. Stoppers and other joints should be adjusted before an apparatus is fixed in the ring stand.

Apparatus with ground-glass joints (Fig. 1.18) are now being frequently used. When work is to be done under vacuum, the ground-glass joints should be lubricated with fat, Vaseline or a special vacuum lubricant, but not too thickly because the lubricant can get into the reaction mixture or the product obtained.

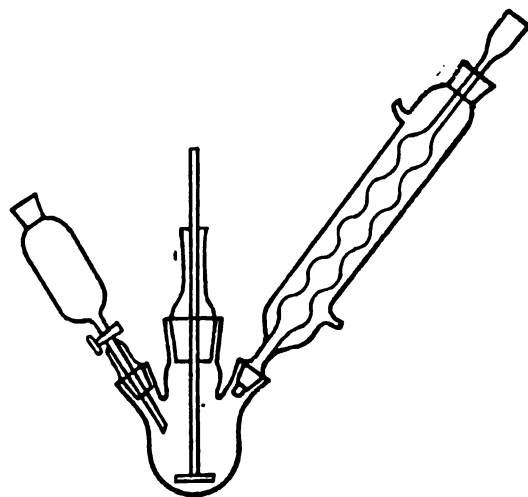


Fig. 1.18. Ground-glass jointed apparatus

Before a stopper is inserted into a flask, the holes in the stopper should be connected to the appropriate apparatus (a dropping funnel, a condenser, etc.). If a rubber stopper is used, its holes should be slightly wetted with glycerol. The stopper is then connected to a vessel, which should not be put on the bench or held by the bottom. The vessel should be held by the neck as close as possible to the place where the stopper is to be inserted; otherwise, the hands can be injured. The stopper should be taken out or put on slowly while twisting it carefully.

When assembling an apparatus, rubber tubing is put on the glass parts. To reduce friction, the tubing should be slightly wetted with water or glycerol. A rubber tube should not be lubricated with oil or Vaseline, because they are absorbed by rubber, which swells and becomes less elastic. When rubber tubing is to be put on a glass tube, the former should be taken by the very end and put on the latter, not straight, but somewhat sideways or un-

derneath. In assembling an apparatus, it must be seen whether its separate parts are tightly and correctly connected. The device should always have access to air in order to preclude a rise in pressure in it as a result of heating or the liberation of gases.

The apparatus is clamped in ring stands after its main parts are assembled. Clamps and paw clutches should have pads so as not to break the assembled device. Flasks should be held by clamps not by the centre of the neck, but near the stopper. Large apparatus should not be fastened too rigidly. Stirrers and dephlegmators should be fixed strictly vertically.

After assembling an apparatus, thoroughly check the assembly.

1.5. CLEANING AND DRYING LABORATORY EQUIPMENT

Laboratory equipment should be clean, because dirt can drastically change the course of synthesis. It should be taken for granted that dirty equipment is to be cleaned immediately after use. In this case, it is necessary to obey the rules given on pages 13-16.

Glassware is clean if drops are not formed and water leaves a uniform thin film on it. Residues can be removed from the vessel sides mechanically, physically, chemically, etc.

If laboratory equipment is not contaminated by resins, fats and other water-insoluble substances, it can be washed with warm water, using brushes. To remove fat residues, it is better to clean the vessels by a stream of water vapour, but this technique takes too long, and therefore it is used rarely. To remove oil distillation products (paraffin, kerosene, wax, oil) and other water-insoluble organic substances from vessels, organic solvents are often used: ethyl ether, acetone, alcohol, gasoline, turpentine, etc. Most organic solvents are flammable liquids, and therefore they should be handled carefully and away from flames. Contaminated organic solvents should be collected and cleaned by distillation (see p. 66).

To clean equipment, use can also be made of soap, a 10 per cent trisodium phosphate solution and modern synthetic detergents. Never use sand for cleaning glassware because it scratches glass, which can break up on heating.

To clean equipment chemically, use is made most frequently of the chromic acid mixture, potassium permanganate, a mixture of hydrochloric acid and hydrogen peroxide, sulphuric acid, and alkaline solutions. The chromic acid mixture is a strong oxidizing agent and is used for cleaning equipment contaminated with tarry and other water-insoluble substances. It is not used for removing oil distillation products and barium salts, which form a barium

sulphate deposit that is difficult to remove. Care should be taken when working with the chromic acid mixture because it acts on the skin and clothes. To prepare the mixture, concentrated sulphuric acid is taken and finely ground potassium dichromate is added in an amount of 5 per cent by weight of the acid. Potassium dichromate is dissolved by carefully heating this mixture in a porcelain dish or a porcelain beaker. After the equipment is washed with the chromic acid mixture, it is rinsed with water, and then the chromic acid mixture heated in a hot water bath to 45-50°C is poured into a vessel up to one-third of its volume and used to wet the vessel sides. The entire mixture is then poured back into the bottle or cylinder where it is kept, and the glassware is washed with warm water. The chromic acid mixture is unfit for cleaning when its colour changes from dark orange to dark green.

A 5 per cent potassium permanganate solution heated to 50-60°C is a very convenient oxidizing agent that is often used for cleaning equipment. The deposit formed on the sides of the vessels after they are cleaned is easily removed

by rinsing the vessels with a 5 per cent sodium bisulphite (NaHSO_3) solution, ferrous sulphate (FeSO_4) solutions as well as with oxalic acid.

A good means for cleaning equipment is a mixture of equal parts of hydrochloric or acetic acid and a 5-6 per cent hydrogen peroxide solution. The mixture is heated to 30-40°C and the vessel walls are washed with it. Then it is poured back into the bottle where it is kept, and the equipment is rinsed with water.

When condensers are used for a long time, a reddish film of iron oxides, which get in with tap water, is formed on the inner surface of the water jacket. To clean the condenser jacket, rinse it with a 10-16 per cent hydrochloric acid solution. When iron oxides are dissolved, the acid is poured out and water is passed through the condenser for 5-10 min.

To clean equipment, concentrated sulphuric acid or alkalies can be used. In this case, all the safety precautions mentioned on pages 14-16 should be taken.

Many organic reactions occur when there are no traces of moisture; therefore, equipment must be dried well after it is thoroughly cleaned and rinsed. Clean equipment is usually dried

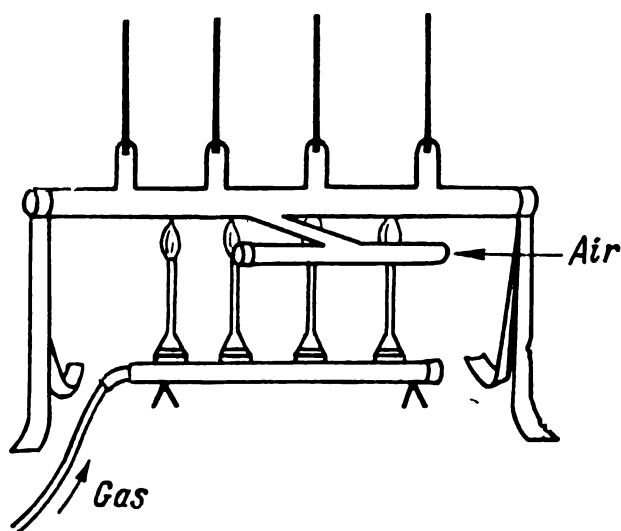


Fig. 1.19. Drier

in a special drying chamber (Fig. 1.19). If the drying chamber is unavailable, equipment should be set in a suitable position and left until it is dry. To quicken drying, air is often sucked through a vessel by means of a bulb and a glass rod, or the equipment is dried in a drying chamber at 80-100 °C.

1.6. LITERATURE, NOTEBOOKS AND REPORTS

A very important aspect of work is homework involving textbooks, study guides, and reference and occasionally original literature. The laboratory should by no means be converted into a reading hall, and laboratory time should not be spent on making the first acquaintance with certain material. Literature can, however, be used in the laboratory when a problem arises in the course of work. A student should make it a rule to carefully read about all aspects of a problem. He should begin homework by preparing theoretical questions involving a certain synthesis with the aid of textbooks and study guides, and then become acquainted with the starting substances used in a given synthesis, i.e., a student should look in reference literature and textbooks for physical constants and data on the properties of these substances, devoting attention especially to the toxicity of the reagents being used. A given synthesis should then be carried out in accordance with a study guide.

A report on every operation must be written, when a certain synthesis is being prepared and carried out. Every report should begin with the date of writing, the experiment number and the name of synthesis. The report must have the equation of the main reaction by which the calculation is being made as well as the equations of side reactions if they occur. It is then necessary to give a brief description of the starting substances and recalculate them if the amounts to be used differ from those given in a study guide, and draw up an experiment plan where all the successive operations to be performed in one synthesis or another are registered.

In describing experiments, a detailed account should be given of the apparatus and the conditions under which reactions are being carried out and their specific features. Everything worthy of attention (a colour change, the appearance of a characteristic odour, etc.) is also noted. It must be kept in mind that the experiment plan and the description of the experiment should by no means be an account of the synthesis methods given in a study guide.

After finishing the experiment, it is necessary to register the amount of the pure product, calculate the yield of a given substance in percentage of the theoretical yield and then describe it. The report ends with the conclusions drawn from the work done. A list of references used is given at the end.

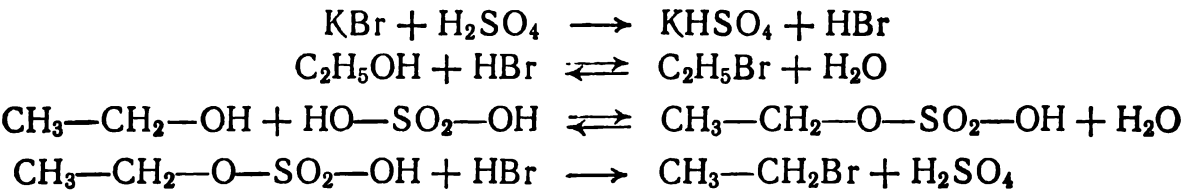
An example of an entry in the laboratory notebook is given below.

Example of an Entry in the Laboratory Notebook

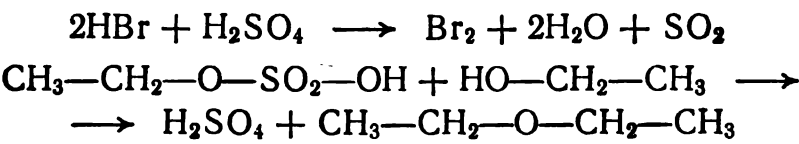
Date Experiment No.

Obtaining ethyl bromide

1. Main reactions:



2. Side reactions:



3. Properties of starting substances and reaction products:

Substance	M	Melting point, °C	Boiling point, °C	Density, d_4^{20}	n_D^{20}	Solubility	Remarks
Ethyl alcohol, 95 per cent	46.07	−114.5	78.4	0.8042	1.3614	Mixes with water, ether and other organic solvents	Vapours with air form explosive mixtures
Potassium bromide	119.02	730	1380	2.7500	—	Dissolves in water and glycerol	—
Sulphuric acid, 95.6 per cent	98.08	10.49 (100 per cent)	338 (partially decomposes)	1.8400	—	Mixes with water	Chars organic substances. It is always necessary to pour acid into water in portions, but not vice versa
Ethyl bromide	109	−119	38.3	1.4586	1.4211	In 100 ml of water at 20 °C, 0.9 g dissolves (this should be taken into account when working); dissolves well in alcohol and ether	

4. Calculation of the amounts of substances needed for synthesis:

(a) according to the study guide, it is necessary to use:

Ethyl alcohol, 95 per cent, ml (mole) . . .	40	(0.7)
Potassium bromide, g (mole)	30	(0.25)
Sulphuric acid ($d = 1.84$), ml (mole) . . .	33	(0.6)

(b) it is necessary to use the following amounts of reagents for 0.1 mole of potassium bromide:

Ethyl alcohol, 95 per cent, ml	16
Potassium bromide, g	11.9
Sulphuric acid ($d = 1.84$), ml	13

5. The theoretical yield of ethyl bromide is 10.9 g.

6. Main stages of synthesis:

- (a) preparation of the reaction mixture and the distillation of ethyl bromide;
- (b) separation of ethyl bromide from water;
- (c) purification of ethyl bromide: removal of ethyl ether and the distillation of ethyl bromide.

7. Sketches of apparatus:

Sketch of apparatus 1 Sketch of apparatus 2

8. Description of the experiment (description of operations, observations and explanations).

9. Yield of pure ethyl bromide:

(a) 8.7 g; (b) 80 per cent of the theoretical yield.

Date of completion of experiment

The instructor's comment and signature

Chapter 2

PRINCIPAL LABORATORY OPERATIONS

Heating and cooling are operations widely used in the organic synthesis laboratory because many reactions in organic chemistry depend on the strict maintenance of temperature conditions.

2.1. HEATING

Most reactions of organic chemistry occur very slowly at room temperature. To accelerate such reactions, the temperature is raised, because it is assumed that the reaction rate usually increases about 2-3 times when the temperature is raised by 10 °C. A growth in the chemical reaction rate upon heating is associated with an increase in the number of collisions between the reacting molecules per unit time and with an increase in the number of active molecules, i.e., molecules which have a greater reserve of energy than others.

In the chemical laboratory, heating can be carried out by electric heaters, gas burners or water vapour. Electric heaters most commonly used are ranges, thermostats, baths, drying chambers, furnaces and flask heaters. In addition, incandescent lamps, which emit infrared rays, are now being used more and more frequently for heating distillation and reaction flasks. Electric flask heaters (closed ones) are usually employed when volatile organic substances are to be heated. It is expedient to use water vapour for heating only when the laboratory can avail itself of vapour from some vapour facility. When reactions are being carried out, the reaction vessel should not be directly heated by electricity or a gas flame because glass is poorly resistant to both sudden changes in temperature and the irregularity of such heating. Local superheating can partially decompose organic compounds. In addition, it is forbidden by safety regulations to heat flammable liquids on an open flame, since they can inflame and even explode if a vessel cracks. The open flame is used mostly in igniting to heat porcelain, fireclay, quartz and other equipment, as well as glazed porcelain dishes for evaporating aqueous solutions or heat-resistant glassware.

An asbestos gauze or a piece of thin sheet asbestos is often used when laboratory equipment is to be heated above 100 °C. In this case, heating is more uniform than on a naked flame. To

maintain the necessary external temperature of heating, use various baths, mostly water, glycerol, oil, paraffin, air and sand baths as well as baths consisting of a mixture of H_2SO_4 and K_2SO_4 (in a ratio of 3:2), low-melting metals, alloys and other materials. In this case, it should be borne in mind that baths must be employed whenever reactions are being carried out at a strictly definite temperature. Baths must be used also in vacuum distillation or when highly flammable liquids are being employed.

Water baths (Fig. 2.1) are used for heating below 100°C . These baths are covered with rings, thus making it possible to select the right size of the bath opening for a vessel to be heated, which is so immersed in water that it does not touch the bottom of the bath.

Oil baths are used when heating is carried out up to 220°C . One-half of a pan or a pot is filled with mineral oils obtained

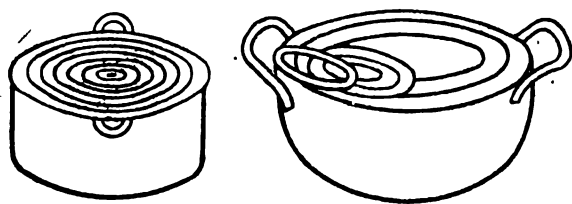


Fig. 2.1. Water baths

from petroleum, while the vessel to be heated is so put into the bath that the substance in it will be on the same level as the oil. The maximum temperature reached by means of such baths depends on the type of oil being used.

When heating is intensive, oils can partially decompose and fume, and therefore work with them is done in a fume cupboard.

Care must especially be taken to prevent water from getting into such baths; otherwise, oil on heating begins to froth and pour out, causing fire. Therefore, reflux condensers should always have a filter-paper collar near their lower end. After finishing work, the surface of a flask should immediately be carefully wiped with a piece of cloth or paper, removing the oil which is still hot. The oil in the bath can inflame when it is being heated for a long time to a high temperature. In this case, neither water nor sand can be used for extinguishing the flames. The bath should be covered with a sheet of asbestos or cold oil should be put into the vessel. During work, the danger of oil catching fire can be reduced by covering the bath with two halves of an asbestos cardboard, cut in the form of a ring to fit the bath with an opening for the vessel to be heated.

Glycerol and paraffin baths are occasionally used instead of oil baths. When glycerol baths are used, heating is performed to a temperature not higher than 200°C , and when paraffin baths are used, not higher than 220°C . The glycerol bath should be heated on an asbestos net instead of an open flame because overheating can cause glycerol to decompose with the formation of lachrymatory acrolein. In other respects, everything which has been

mentioned about oil baths applies to glycerol and paraffin baths as well.

The simplest air bath is Babo's funnel (Fig. 2.2), which is heated by a gas burner. It consists of a tin cone with several asbestos strips attached to its inner wall to prevent the vessel to be heated from touching the hot tin. A tin plate, which prevents the bottom of the flask from directly touching the flame, is fixed at the lower part of the cone. Air baths allow heating practically to any temperature, but such heating is less uniform.

When substances are being heated to 325 °C, use can be made of baths consisting of a mixture of H_2SO_4 and K_2SO_4 , to 400 °C, sand baths, and to 600 °C and higher, baths consisting of low-melting metals and alloys. All precautions must be taken in heating. *Safety spectacles should be put on when working with substances which can splash on heating.*

When flammable liquids (ether, acetone, benzene, alcohol and others) are used, the water bath should first be heated at some distance from the device. The burner should then be turned off and the vessel with a flammable liquid to be heated should gradually be immersed in the bath. The vessel containing liquid should be so immersed in the bath that its content will be on the same level with the water in the bath. In addition, it should be borne in mind that water baths cannot be employed when metallic sodium and metallic potassium are used. When liquids are heated above the boiling point, superheating and even an explosion can occur. This can be precluded by using boiling stones, i.e., chips of roasted unglazed porcelain, small pieces of brick or long glass capillary tubes sealed at one end. The capillary tubes are put by their open ends into the liquid, while their other ends should protrude from the liquid and be in the flask neck. On heating, boiling stones or capillary tubes release a small amount of air in the form of tiny bubbles and ensure mixing and uniform boiling. In this case, they must be put only into cold liquid. They should by no means be put into boiling liquid since the liquid can spurt from the flask as a result of sudden vapour formation. Before resuming distillation which has been interrupted, it is necessary to turn off the burner and add more boiling stones to the cooled flask because the liquid fills all the pores of the old boiling stones on cooling and they become ineffective.

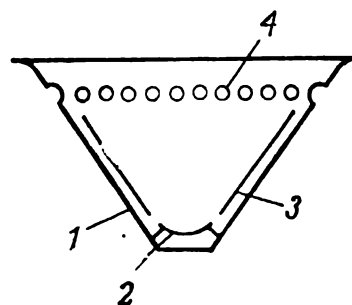


Fig. 2.2. Babo's funnel:

1—tin cone; 2—tin plate which partially closes the lower opening of the funnel; 3—asbestos strips; 4—outlet for hot gases

2.2. COOLING

When exothermal reactions are being carried out, the reaction mixture can be overheated as a result of the evolution of a large amount of heat. This can reduce the product yield. In such cases, the mixture must be cooled.

The cheapest and the most convenient coolant is tap water, whose temperature ranges from 4 °C to 20 °C, depending on the season. The reaction vessel is usually cooled by putting it in running tap water or regularly immersing it in cold water. If the reaction flask is to be cooled in an apparatus, it is put in a large funnel with a hose and running water is poured on it. To condense the vapours as they are cooled, use is made of various types of condensers (see Fig. 1.6) with cold water circulating in their jackets.

For cooling to 0 °C, use ice crushed to the dimensions of a walnut. For cooling to temperatures below 0 °C, cooling mixtures are used. To obtain a temperature from approximately -5 °C to -20 °C, use a mixture of ice and common salt that consists of three parts finely crushed ice and one part commercial common salt. Lower temperatures (down to -50 °C) can be obtained by using a mixture of five parts crystalline calcium chloride and four parts finely crushed ice. A temperature as low as -70 °C can be obtained by using solid carbon dioxide (dry ice). By mixing solid carbon dioxide with absolute ethyl alcohol, we can obtain a temperature as low as -72 °C; with ether, as low as -77 °C, and with acetone, as low as -78 °C.

Dry ice should preferably be crushed in a metallic mortar, and safety spectacles should be put on. Dry ice should be put carefully into alcohol, acetone and ether because there is intensive frothing in this case. If the foregoing mixtures are inadequate as coolants, liquid air and liquid nitrogen are used for cooling.

2.3. MEASURING AND CONTROLLING THE TEMPERATURE

Mercury thermometers are usually used for measuring the temperature of a reaction ranging from -35 °C to +350 °C. Mercury thermometers filled with nitrogen can be used for measuring the temperature within the 350-600 °C range. Thermometers filled with coloured toluene or alcohol are used for checking temperatures ranging from -35 °C to -60 °C. High temperatures are measured by thermocouples. The thermometer is usually put into the reaction mixture or the bath. It should always be put into oil, glycerol and paraffin baths because, unlike a boiling water bath, they do not have a constant temperature. The temperature can be somewhat

controlled by limiting the supply of heat to a bath, i.e., by changing the size of a gas flame or switching on an electric heater through a resistor. To set the voltage, use can be made of a laboratory autotransformer, a single-phase voltage regulator and special regulators.

2.4. GRINDING AND STIRRING

Solid materials can be ground either manually or by means of various crushers, mills, grinders, etc. For manual grinding, use is made of various mortars: steel, cast-iron, bronze, porcelain, agate and others. Porcelain mortars (see Fig. 1.13c) are most commonly used in the organic synthesis laboratory. One-third of the mortar is filled with the substance to be ground, and then large pieces are carefully crushed to the size of a pea with a pestle and then ground. When harmful substances and substances

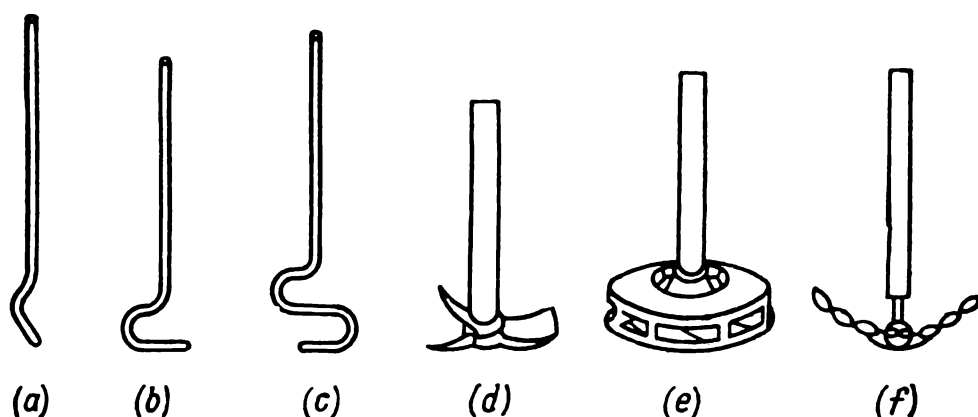


Fig. 2.3. Stirrers:

a, b, c—glass; d—metallic paddle; e—metallic centrifugal; f—Hersberg metallic

which raise much dust are to be ground, work should be done in a fume cupboard.

Stirring is an important operation which not only accelerates a reaction, but also makes it possible to carry it out. It is very important to stir a reaction mixture well when one of the reagents is insoluble and also when a reagent is being gradually added to the reaction mixture. As a result of stirring, a substance is rapidly and uniformly distributed throughout a solution, thus precluding local superheatings and an increase in concentration. It is often enough to stir the mixture manually or shake the reaction vessel when work is being done with small amounts, and when a reaction is occurring rapidly and being carried out in open vessels. Various stirrers (Fig. 2.3) are used when work is being done with large amounts and when reactions occur for a long time.

The effectiveness of stirring largely depends on the structure of the stirrers. Stirrers made out of thick glass rods

(Fig. 2.3*a, b, c*) are often used. They are very convenient because they can be given any shape before an experiment, depending on the size of the reaction vessel, the width of the neck and other requirements under given conditions. Metallic stirrers (Fig. 2.3*d, e*) are used for stirring large quantities, and Hershberg stirrers (Fig. 2.3*f*), for stirring heavy precipitates or viscous liquids.

Stirrers are usually put into motion by electric motors (Fig. 2.4*a*), which can be secured in a stand as well as on special wooden props. The rate of the motor's rotation should be controlled by a rheostat or a regulating transformer. To see whether the

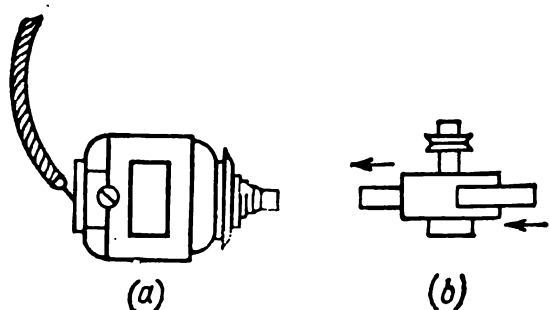


Fig. 2.4. Motors for stirrers:
a—electric motor; *b*—hydraulic turbine

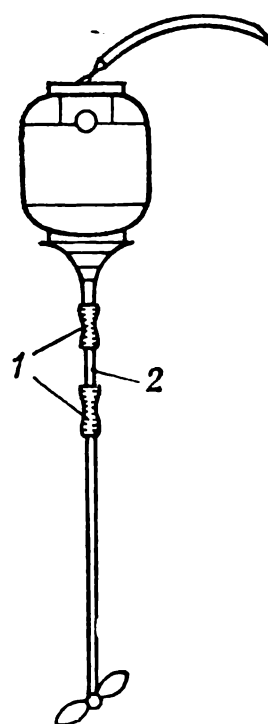


Fig. 2.5. Attaching a stirrer to the electric motor by two pieces of a vacuum hose:
1—pieces of a vacuum hose; *2*—glass rod

motor is jammed and to be sure that it will touch neither the sides of the vessel nor the thermometer when in operation, its stirrers should be turned manually before switching it on. Many electric motors have a coupling sleeve for the stirrer. To prevent the stirrer from slipping when the motor has no sleeve, connect it to the shaft by two pieces of a vacuum hose and a glass rod (Fig. 2.5). In this case, it should be seen to that the shafts of the electric motor and of the stirrer form a straight line.

When work is being done with highly flammable substances (e.g., carbon disulphide and ether), electric motors with a long flexible hose can be employed, but it is more expedient to use hydraulic turbines (Fig. 2.4*b*). For a hydraulic turbine to operate, it should be secured on a stand and one of its arms should be

connected by a hose to a water faucet, while a drainage tube should be put on the other arm and lowered into the sink. The turbine begins to operate as the water faucet is opened, and the rotation of the turbine rotor is controlled by the intensity of the water jet (Fig. 2.6).

Magnetic stirrers are used in hydrogenation, for work under high vacuum and in some other cases.

If a stirrer is to operate uniformly and noiselessly, the position of its axis should be well fixed. To this end, ordinary stirrers are assembled in the following way: the stirrer rod is put into a glass tube, lubricated with Vaseline or glycerol, which acts as a bearing.

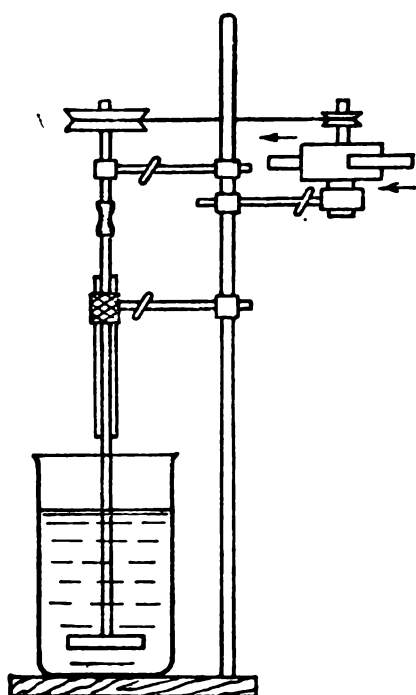


Fig. 2.6. Hydraulic turbine in operation

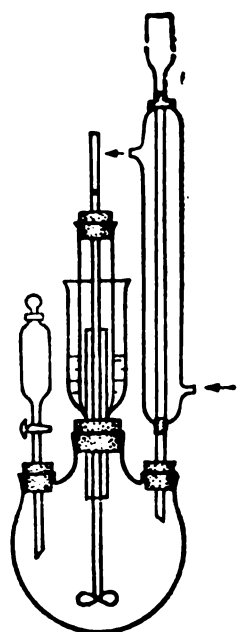


Fig. 2.7. Stirrer with a mercury seal

This tube is inserted into a rubber or cork stopper, which is clamped in the ringstand. A grooved wooden pulley is put on the upper end of the stirrer by means of a short rubber tube and is connected by a belt to the shaft of a turbine or an electric motor (see Fig. 2.6).

Seals are used when the reaction mixture has to be isolated from the action of moisture or air. The simplest and the most common way of sealing the stirrer is by connecting its rod to the bearing by a small rubber tube. To reduce friction in such cases, the inside of the rubber tube is lubricated with Vaseline, while the bearing is connected to the reaction vessel by a stopper. Airtightness is practically guaranteed when a mercury seal (Fig. 2.7) is used.

A glycerol layer on mercury will serve as protection from harmful mercury vapours. In laboratories for students, it is better to use glycerol seals instead of mercury ones.

2.5. DISSOLUTION AND PROPERTIES OF SOME ORGANIC SOLVENTS

Dissolution is the formation of a solution (a clear homogeneous mixture) when a substance (gas, liquid or solid) mixes with a liquid known as the solvent. The main condition for this process is that there should be no chemical interaction between a solute and a solvent. Consequently, the dissolved substance should remain unchanged when the solvent is removed.

The dissolution of solids and liquids is always connected with the consumption of energy, i.e., with the absorption of heat because the molecules of a substance are distributed in a large volume. An opposite phenomenon, the evolution of heat, is observed when gases dissolve; this is due to a reduction in the volume in which the molecules of a gas are distributed. But the evolution of heat is often observed when solids and liquids dissolve, indicating that the heat of hydration of a given solid is greater than that of dissolution of the corresponding hydrate.

The rate of dissolution of a solid depends on the size of its particles. The finer the individual particles of a substance, the larger the liquid-solid interface and, consequently, the more rapid the dissolution. But occasionally, when a finely ground substance is poured into water, it does not become wet and floats on the water surface. In such cases, the powder is moistened with a small amount of pure alcohol and then poured into water. Of course, alcohol can be used only if it does not act chemically on the substance or its solution.

The solubility of a solid can often be increased by heating the solution. But it should then be taken into account that this rule cannot be applied to some salts, whose solubility either decreases or slightly increases with an elevation of temperature.

Almost all gases are capable of dissolving to a certain extent in water or organic solvents. For instance, ammonia and hydrogen chloride are absorbed well by water, while oxygen and hydrogen are less soluble in water. Gases usually become less soluble in liquids as temperature rises or pressure drops. Therefore, in order to remove a dissolved gas, liquid is usually heated or evaporated under vacuum.

In the chemical laboratory, dissolution is used for many purposes: for obtaining a homogeneous medium, i.e., for creating more favourable conditions which provide the largest interface of

the reagents; for separating substances and purifying the reaction products by recrystallization; for changing the rate or direction of a reaction; for carrying out reactions without water, etc.

Solutions can be either aqueous or non-aqueous. Aqueous solutions are those of most salts, alkalies and acids, while non-aqueous solutions are solutions in organic solvents, e.g., alcohols, ethers and acetone.

Organic solvents are widely used for dissolving organic liquids and solids, such as oils, fats and resins. They are also used for dissolving inorganic substances and carrying out non-aqueous titration in analytical chemistry. In the laboratory, use is usually made of pure organic solvents obtained by purifying inexpensive commercial products.

Many organic solvents are *flammable and poisonous*. Therefore, all precautions should be taken when working with them.

ETHYL ALCOHOL

Ethyl alcohol (95.6 per cent, rectified spirit) has a b.p. of 78.3 °C and d_4^{15} of 0.7936, and is a constantly boiling azeotropic mixture containing 4.4 per cent of water. It is necessary for many purposes to use 100 or 99.9 per cent ethyl alcohol, known as absolute alcohol, which was first obtained by the Russian academician Lovits. Water in ethyl alcohol cannot be removed by simple distillation. In the laboratory, alcohol can be dehydrated by being heated with readily hydrating substances, such as calcium oxide or anhydrous cupric sulphate. Dehydrated 99.5 per cent ethyl alcohol is obtained by means of calcium oxide and anhydrous cupric sulphate in a flask with a reflux condenser that has a calcium chloride tube for protecting alcohol from humidity. Commercial calcium oxide, being in the form of pieces with dimensions of a filbert, is roasted in an electric furnace for 1-2 h before use. When calcium oxide cools, it is immediately put in a bottle with a tight fitting lid.

A one-litre round-bottom flask is filled with 500 ml of 95.6 per cent ethyl alcohol and 125 g of freshly ignited calcium oxide. The mixture is boiled in a water bath for six hours and then left overnight. During this time, most of the pieces of calcium oxide become powdery calcium hydroxide. After cooling, alcohol is distilled in an apparatus for distilling dry low-boiling solvents; in this case, the receiver is a bottle in which the absolute alcohol is to be kept (Fig. 2.8). Alcohol is distilled at first in a low-boiling water bath to which a small amount of common salt has been added, and then in a boiling bath. The initial 15 ml of distillate are discarded. Distillation occurs rather slowly and a substantial amount of alcohol is retained by the solid residue. Such treatment

makes it possible to bring the purity of alcohol to 99.5 per cent, which is enough for most operations.

Alcohol is dehydrated by cupric sulphate in the following way: the crystal hydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is heated while being mixed in a nickel or porcelain dish to 220°C until it turns into a white powder. The dehydrated cupric sulphate obtained is cooled and added to alcohol in an amount of 200-250 g per litre of alcohol. The mixture is boiled for six hours with a reflux condenser having a calcium chloride tube and left overnight. On the next day, it is distilled (see Fig. 2.8). Such treatment is repeated again. For dehydrating alcohol, use cannot be made of calcium chloride and sulphuric acid, because the former forms with alcohol a crystal hydrate, while the latter, esters.

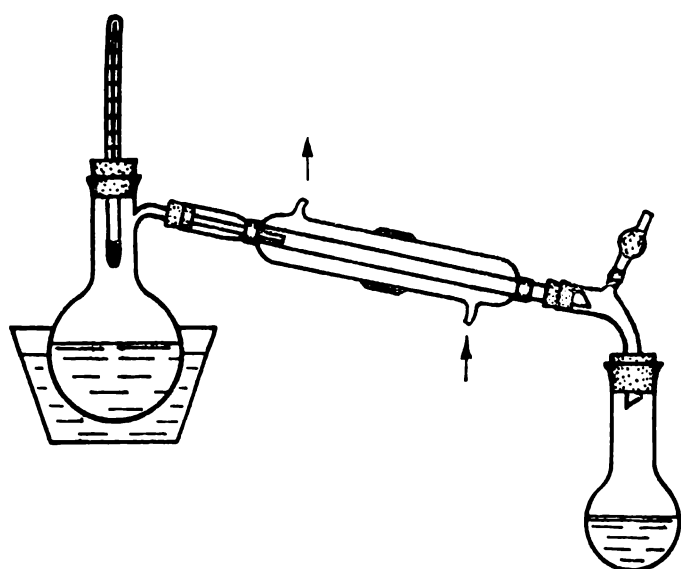
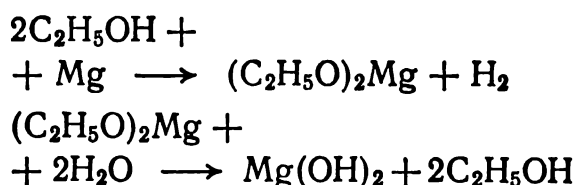


Fig. 2.8. Apparatus for distilling dry low-boiling solvents

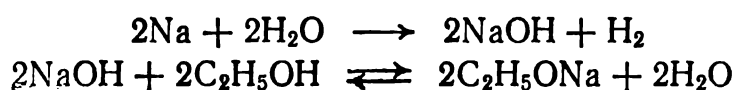
To obtain anhydrous absolute ethyl alcohol, use can be made of magnesium and sodium; alcohol is now usually dehydrated by an azeotropic mixture with benzene. Let us consider these cases.

Action of Magnesium:



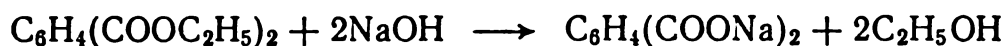
Five grams of magnesium chips and 0.5 g of iodine are put into a two-litre round-bottom flask having a reflux condenser with a calcium chloride tube, and 70-75 ml of dehydrated ethyl alcohol are added. The mixture is heated until the iodine colour disappears. Afterwards, 900 ml of dehydrated ethyl alcohol are poured into the flask and the mixture is boiled for 30 min. The flask is then cooled, the reflux condenser is replaced by a downflow condenser, a receiver is connected to it by means of a bent adapter with an outlet linked to the calcium chloride tube for protection from moisture, and the mixture is distilled. When all the precautions against moisture are taken, 99.95 per cent alcohol is obtained.

Action of Sodium. Sodium readily reacts with the water in alcohol and partially with the alcohol. The sodium hydroxide formed undergoes alcoholysis in which equilibrium is established between sodium hydroxide and alcohol on the one hand, and their interaction products, i.e., sodium ethoxide and water, on the other:



The sodium hydroxide formed can be made to irreversibly react with the excess high-boiling ester by treating it with diethyl phthalate.

In the subsequent distillation from the flask with a small dephlegmator, ethyl alcohol is easily driven off from the ester:



A two-litre round-bottom flask is provided with a reflux condenser to which a downflow condenser with, as we have seen, a receiver is connected by means of a bent adapter. One litre of dehydrated alcohol and seven grams of pure dry sodium are put into the flask. After sodium reacts, 30 g of diethyl phthalate are added and the reaction mixture is boiled uniformly for two hours. Water is then discharged from the sleeve of the reflux condenser and alcohol is distilled in a water bath, using the reflux condenser which is uncooled by water as a headpiece.

Dehydration of Alcohol by an Azeotropic Mixture with Benzene. Azeotropic, or constant boiling, solutions are distilled without a change in their composition and boiling point, i.e., they cannot be decomposed by simple distillation. In 1884, D. P. Kononov showed that azeotropic mixtures exist in systems in which the dependence of a solution's vapour pressure on its composition at constant temperature, or the dependence of the boiling point on the composition at constant pressure, is expressed by curves having minima or maxima. In this respect, there are azeotropic mixtures with (a) a boiling-point minimum (with a vapour-pressure maximum) and (b) with a boiling-point maximum (with a vapour-pressure minimum).

Multicomponent mixtures, like binary ones, often have azeotropic points which are characterized mainly by a pressure maximum and a boiling-point minimum. The minimum of the boiling point of ternary mixtures is observed when all three or at least two binary mixtures containing the same components have boiling-point minima. In this case, the minimum of the boiling point of ternary mixtures is deeper than that of binary mixtures consisting of the same components. For instance, three binary mixtures can be formed from the components of a ternary mixture consisting of alcohol, benzene and water: (1) alcohol-water; (2) benzene-water, and (3) alcohol-benzene. The minima of the boiling points of these mixtures are 78.2°, 69° and 68.3 °C, respectively, while the ternary mixture boils at an even lower temperature: 64.9 °C.

This property of a ternary azeotropic mixture can occasionally be used for separating binary mixtures having azeotropic points. For instance, to dehydrate $\text{C}_2\text{H}_5\text{OH}$, i.e., to distil pure ethyl alcohol from a binary mixture of ethyl alcohol and water, it is enough to add the amount of benzene needed for forming a ternary mixture

to the mixture. Absolute ethyl alcohol can be distilled because a ternary mixture was formed when benzene was added. This mixture has a deeper boiling-point minimum and contains, in its azeotropic point, more water than the azeotropic mixture of ethyl alcohol and water. In azeotropic rectification, a third component is often added for separating binary azeotropic mixtures.

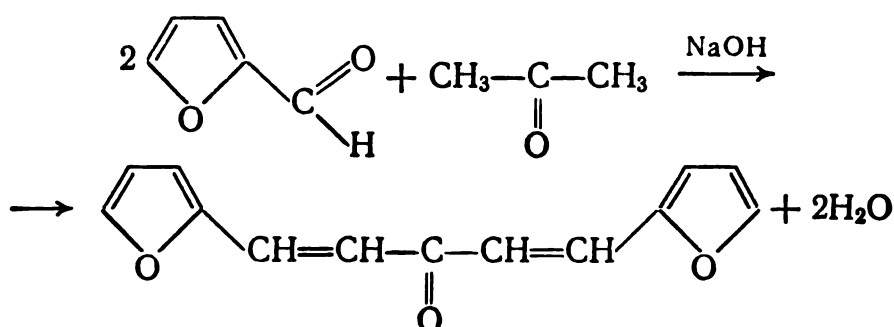
The water content of the absolute alcohol obtained is ascertained by determining its density and finding the composition corresponding to it in the table of any handbook. Absolute 99.95-100 per cent ethyl alcohol is very hygroscopic, and therefore it should be kept in a bottle with a well ground stopper.

Ethyl alcohol is a narcotic. Its prolonged action causes serious diseases of the cardiovascular system, the digestive tract, etc.

METHYL ALCOHOL

Synthetic methyl alcohol with a b.p. of 64.7 °C and d_4^{15} of 0.7961 can be used for most operations. It usually contains 1-2 per cent of water, traces of acetone (up to 0.1 per cent) and formaldehyde.

A convenient method of removing acetone is by heating a mixture of 500 ml of methyl alcohol, 25 ml of furfural and 60 ml of a 10 per cent aqueous solution of sodium hydroxide with a reflux condenser for 6-12 h; a resin containing difurfural acetone and other high-boiling substances is then formed:

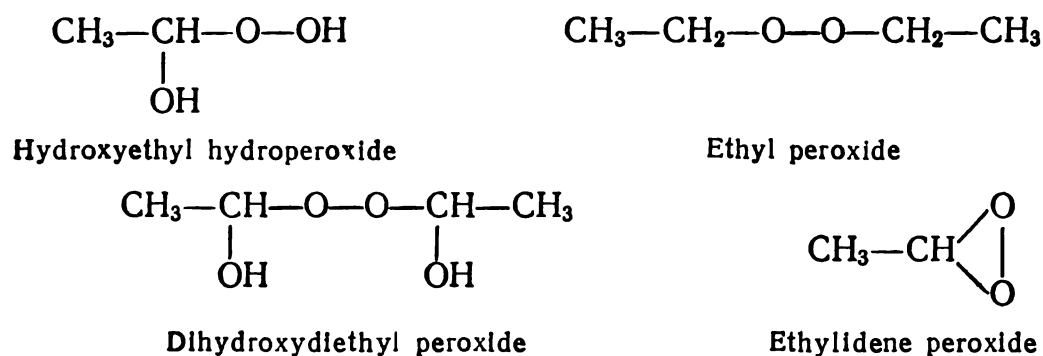


Methyl alcohol is then distilled with a dephlegmator (see Fig. 1.11) or on a column, discarding the initial 15-20 ml, which contain formaldehyde traces. *All safety precautions must be taken when methyl alcohol is being used because it is highly flammable and forms explosive mixtures with air.* Moreover, it should be borne in mind that *methyl alcohol is very toxic*: a long inhalation of its vapours causes poor eyesight, irregular heart beat and loss of consciousness. Even small doses taken orally causes blindness and death.

ETHER

Commercial ether with a b.p. of 34.6 °C and d_4^{15} of 0.7192 contains a small amount of water and ethyl alcohol. When it is kept for a long time in the light and is unprotected from air, it slowly

oxidizes with the formation of aldehydes, acids and unstable explosive peroxide compounds:



It should be taken into account that all ethers (especially diisopropyl ether) form peroxides. Great explosions caused by the distillation of unrectified ether often occur in laboratories. Therefore, it is necessary to check whether *ether has peroxide compounds* before using it.

Peroxides can be detected by shaking several millilitres of ether with the same amount of a 2 per cent potassium iodide (or sodium iodide) solution acidified with a few drops of hydrochloric or sulphuric acid. Peroxides are present if the ether layer turns brown somewhat later.

Another technique of detecting peroxides is by dissolving 1 ml of sodium dichromate in 1 ml of water, adding a drop of dilute sulphuric acid and an ether sample and shaking the mixture. Peroxide compounds are present if the ether layer turns dark blue.

Peroxides can be removed from ether by several techniques. The simplest one is by shaking ether with powdery potassium hydroxide (70 g of potassium hydroxide per litre of ether). Another technique is by washing ether with a ferrous sulphate solution. To wash one litre of ether, it is enough to use 10-20 ml of a solution consisting of 60 g of crystalline ferrous sulphate, 6 ml of concentrated sulphuric acid and 110 ml of water. Peroxides can also be removed by shaking one litre of ether with 20-25 ml of a sodium sulphite solution saturated in the cold in 50 ml of water. After settling, ether is removed and washed with a 0.5 per cent potassium permanganate solution so as to convert the acetaldehyde formed into acetic acid. The ether separated is then washed with a 5 per cent sodium hydroxide solution and water and dried for a day, adding 150-200 g of granulated calcium chloride per litre of ether. Calcium chloride is then filtered off through a folded filter, while ether is collected in a dark bottle with a cork stopper, at the same time making sure that all the nearby burners are turned off.

To obtain absolute ether, 5 g of finely cut metallic sodium per litre of dry ether are put in the bottle containing the ether. The bottle is tightly closed with a cork stopper into which a calcium chloride tube is inserted. After allowing the mixture to stand for

24 h, another 2.5 g of sodium are added and, in 12 h, the ether is poured into a dark bottle which has a good cork stopper. To protect the ether from peroxide formation, add to it an insignificant amount of either diphenylamine or phosphoric anhydride, or several pieces of copper wire.

Ether is a highly flammable solvent, and therefore *it must be seen to that the place where the ether is being handled is at least three meters away from flames*. The ether should be poured by means of a small funnel with a wide stem; its distillation must be performed in a water bath in a device for distilling low-boiling anhydrous solvents (see Fig. 2.8).

Ether is a narcotic and irritates the respiratory tracts.

PETROLEUM ETHER

Petroleum ether is a petroleum fraction which boils at 40-70 °C. It contains unsaturated and aromatic hydrocarbons. It is purified by shaking for 20 min with two or three portions of concentrated sulphuric acid (100 ml of the acid per litre of petroleum ether). After the lower acid layer is removed, the ether is washed in a separatory funnel with a few portions of a concentrated solution of potassium permanganate in a 10 per cent sulphuric acid solution until the water layer acquires a stable violet colour. Petroleum ether is then washed with water, a 10 per cent sodium hydroxide solution and again with water, dried with anhydrous calcium chloride like ether (see p. 45), and distilled (see Fig. 2.8) in a water bath with closed electric heating. The ether obtained is stored over metallic sodium.

Petroleum ether forms with air explosive mixtures and has a low flash point; therefore, care should especially be taken when working with it. Petroleum ether vapours can cause poisoning.

ACETONE

Pure acetone with a b.p. of 56.2 °C and d_4^{20} of 0.7908 can be isolated from commercial acetone, which contains water, methyl alcohol and acetic acid. Several techniques can be used for purifying commercial acetone and obtaining absolute acetone. One of them is by heating acetone with powdery potassium permanganate. Commercial acetone (1 lit) is put in a flask with a reflux condenser and 6-7 g of powdery potassium permanganate are added in portions. The mixture is boiled for 5-6 h in a water bath until the liquid acquires a stable colour. The reflux condenser is then replaced by a downflow condenser; acetone, which has already been isolated from methyl alcohol but still contains water, is driven off. For drying, the reflux condenser is closed with a calcium chloride tube,

anhydrous calcium chloride (120 g per litre of acetone) is put into the flask, and the mixture is boiled for 4-5 h in a water bath. On cooling, acetone is rapidly poured onto fresh calcium chloride and boiled again for 4-5 h. The reflux condenser is then replaced by a downflow condenser (Fig. 2.8) and acetone is driven off into an ice-cooled receiver made of brown glass.

Another technique of purifying acetone is by obtaining a compound of acetone and sodium iodide ($\text{NaI} \cdot 3\text{CH}_3\text{COCH}_3$), which decomposes on heating with the isolation of acetone. One hundred grams of pure, finely ground sodium iodide are put in a flask with a reflux condenser, 400 ml of acetone are added, and the mixture is boiled in a water bath until the precipitate completely dissolves. The solution is then cooled to -8°C with a mixture of ice and salt, the crystals formed are filtered off on the Büchner funnel, the solution is put into a distillation flask connected to a downflow condenser, and acetone is distilled by slight heating into an ice-cooled receiver.

Safety precautions should be taken when working with acetone, because it is *highly flammable* and forms *explosive mixtures* with air.

Acetone is *toxic*, and its vapours irritate the upper respiratory tracts.

2.6. DRYING AND PRINCIPAL DRYING AGENTS

Drying is the liberation of a substance in any state of aggregation from any impurity of a liquid. In most cases, drying implies the removal of moisture or organic solvents.

Many reactions in organic chemistry are carried out without moisture. In such cases, the starting substances should be dried, dehydrated solvents should be used, and the reaction medium should be protected from humidity. The drying agent should act rapidly, and should not dissolve in organic liquids and interact with the substance being dried.

DRYING GASES

Most gases obtained in the laboratory, and also many compressed gases contained in cylinders, can be dried with concentrated sulphuric acid or solid drying agents, such as calcium chloride, soda lime and phosphoric anhydride (or phosphorus pentoxide).

Sulphuric acid can be used to dry air and the following most frequently employed gases: oxygen, hydrogen, nitrogen, carbon monoxide and dioxide, chlorine, hydrogen chloride and sulphur dioxide. To dry a gas, pass it through Drexel, Tishchenko or

Alifanov wash bottles filled to one-third of their volume with concentrated sulphuric acid (Fig. 2.9). A wash bottle is usually con-

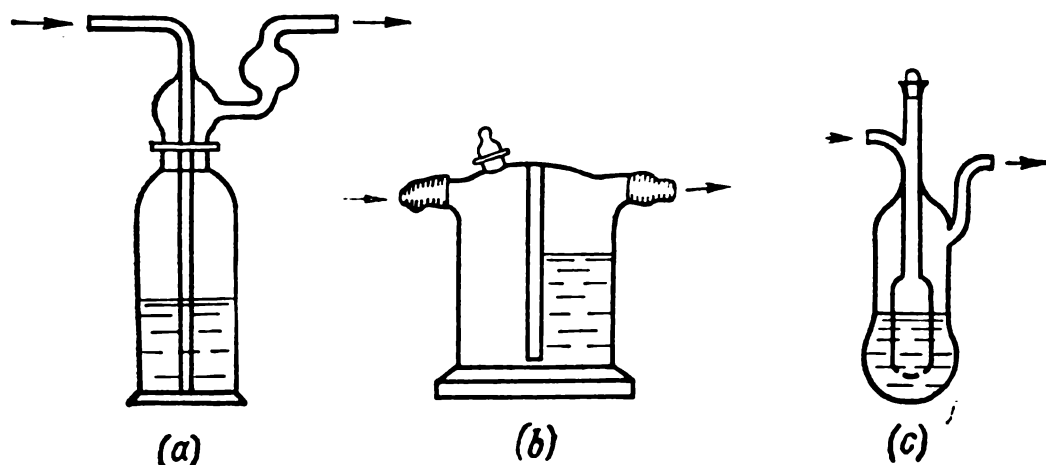


Fig. 2.9. Wash bottles:
a—Drexel bottle; b—Tishchenko bottle; c—Alifanov bottle

nected to a gas source and an apparatus by means of two empty safety flasks. Use the Drexel or Tishchenko bottles for this (Fig. 2.10). Gases are dried with solid drying agents in drying

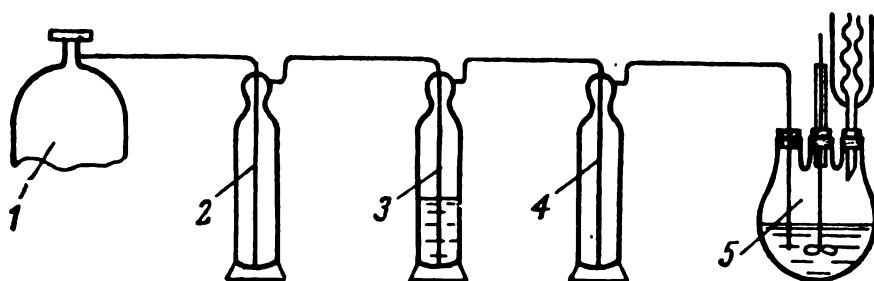


Fig. 2.10. Scheme of the apparatus for introducing a gas into the reaction vessel:
1—gas cylinder; 2, 4—safety flasks; 3—wash bottle; 5—reaction vessel

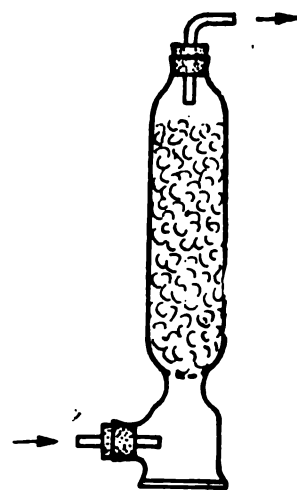


Fig. 2.11. Drying column

columns (Fig. 2.11), and the apparatus is closed with a calcium chloride tube (see Fig. 1.12) to protect a gas from humidity.

DRYING ORGANIC LIQUIDS

Organic liquids are usually dried with solid inorganic drying agents. In this case, a small amount of the latter is taken to preclude losses due to the adsorption of a substance by a drying agent. At first, an organic liquid is shaken with a small amount of drying substance (up to 3 per cent of the mass of the solution),

Somewhat later, a small layer of an aqueous solution of the drying agent is formed if, for drying, use was made of substances which form hydrates with water (calcium chloride, sodium sulphate, sodium hydroxide, magnesium sulphate). The liquid is then poured out and another portion of the drying agent is put in. This is repeated until the drying agent no longer absorbs water, e.g., calcium chloride no longer deliquesces and phosphoric anhydride no longer sticks together. After such treatment, the organic liquid is put into a flask which is closed with a stopper having a calcium chloride tube, and left overnight with another portion of a drying agent. Prior to distillation, the dried organic liquid is filtered off or, most frequently, decanted.

DRYING SOLIDS

Highly volatile impurities can be removed from nonhygroscopic solids by drying the solids on filter paper, while thermally stable substances can be dried in drying chambers. Ordinary and vacuum desiccators (Fig. 2.12) are often used for drying solids. Vacuum

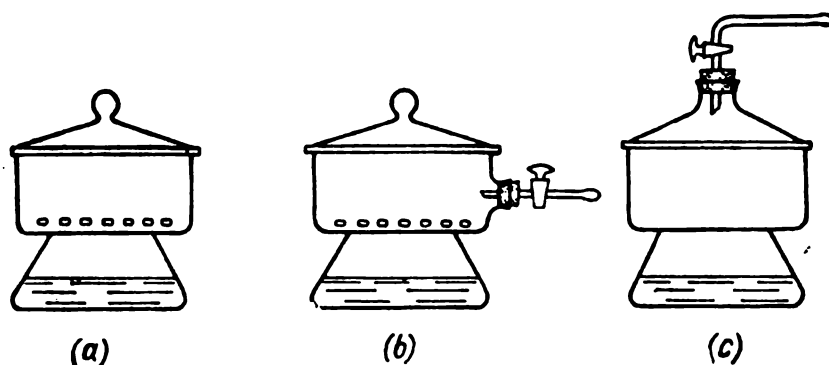


Fig. 2.12. Desiccators:
a—ordinary; b, c—vacuum

desiccators have an opening through which a tube with a stopcock on a rubber stopper is put. This makes it possible to connect the desiccator to a water pump. A manometer and a safety flask are put between them (Fig. 2.13).

Desiccators occasionally *explode* under vacuum, and therefore *they must be wrapped in a towel before the pump is switched on*. When opening the vacuum desiccator, the stopcock should be turned very carefully and slowly so as to prevent the dried substance from being sprayed by air. Open the ground-glass lid of the vacuum desiccator only when the pressure is uniform.

The drying agent is selected in conformity with the chemical properties of the substance to be dried. The drying agents most commonly used for desiccators are calcium chloride, soda lime, caustic alkali bases, phosphoric anhydride, and concentrated sulphuric acid. In this case, it should be borne in mind that sulphuric

acid cannot be used for vacuum drying; it is employed only in ordinary desiccators for absorbing moisture, the residues of alcohol, ether, acetone, aniline, and pyridine. Paraffin is used as a desiccator filler for adsorbing hydrocarbons, especially hexane, ligroin, benzene and its homologues. Caustic alkali bases are used for removing acid substances. Phosphoric anhydride and soda lime absorb water and alcohol well.

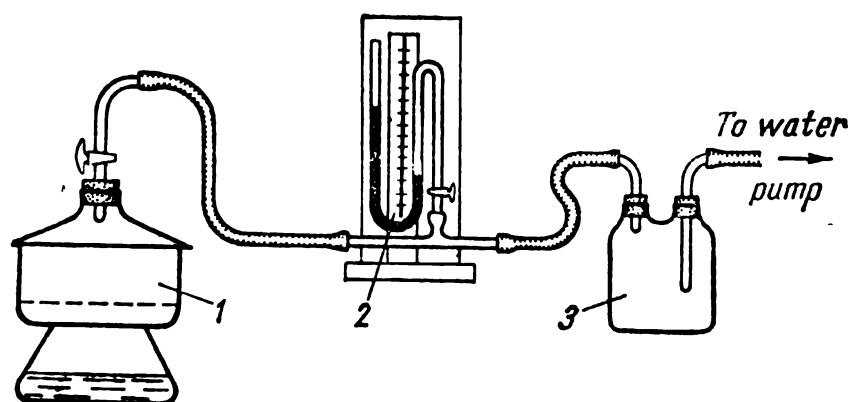


Fig. 2.13. Scheme of connecting the vacuum desiccator to the water pump:
1—vacuum desiccator; 2—manometer; 3—safety flask

PRINCIPAL DRYING AGENTS

Anhydrous calcium chloride is the cheapest, most commonly used drying agent with a great intensity for drying. It dries slowly, however, and is unsuitable for drying alcohols, phenols, amines, amino acids, amides, acid nitriles, esters, and some ketones and aldehydes because it forms compounds with them. In addition, calcium chloride contains lime as an impurity; therefore, it cannot be used for drying acid substances. It is employed as a preliminary agent for drying saturated, ethylene hydrocarbons, acetone, ethers and other compounds to rid them of water.

Anhydrous magnesium sulphate is one of the best drying neutral agents that rapidly absorbs water and has high absorptivity. It is used for drying the greatest number of compounds.

Anhydrous sodium sulphate is an inexpensive neutral drying agent used for preliminarily removing large amounts of water; but it acts slowly and does not bind all the water. It cannot be employed for drying benzene, toluene and chloroform.

Alkali bases (sodium hydroxide and potassium hydroxide) are good, rapid drying agents, but their application is very limited, being confined only to amines and ethers.

Absorbent cotton dried beforehand in a drying chamber at 100°C is an excellent drying agent and is employed in calcium chloride tubes.

Supplement 1 gives the drying agents used for drying different classes of organic compounds.

2.7. FILTRATION

In the laboratory, filtration is usually used for mechanically separating the solid and liquid components of a mixture. But in the simplest case, a liquid can be poured off a precipitate which has settled. This process is known as decantation. It is expedient to use both techniques, i.e., first, a liquid should be separated and the precipitate washed several times by decantation, and this followed by filtration.

Washing by decantation is done by first covering the precipitate with water or a specially prepared wash liquid. Then the mixture is stirred with a stirring rod and allowed to settle. Afterwards, the liquid is carefully (so as not to spray it) poured off the precipitate by a stirring rod on a filter in a funnel; in this case, the precipitate should remain in the vessel (Fig. 2.14). The precipitate is washed several times. Decantation makes it possible to wash the precipitate off the mother liquor more thoroughly; this cannot be done always in filtration, because the precipitate cakes readily. Washing should be done with as small an amount of liquid as possible because there are no absolutely insoluble substances, and every time a fresh portion of a liquid is used for washing, a part of the precipitate, though insignificantly small, passes into solution. In washing the precipitate, the liquid should be poured on the filter in an amount that will completely cover the precipitate and will not reach the edges of the filter by 3-5 mm. In addition, another portion of liquid should be poured on the filter after the last portion is completely filtered off.

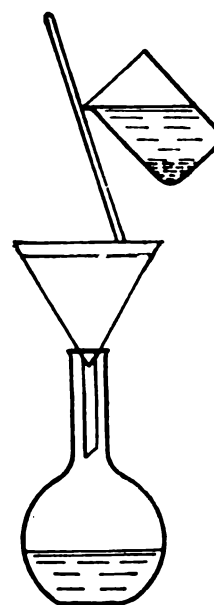


Fig. 2.14. Decanting liquid by a stirring rod

Filtration is characterized by rapidity and thoroughness in separating the precipitate from the liquid. The effectiveness of filtration is determined by the following factors:

- (1) viscosity (the higher the viscosity of a solution, the more difficult it is to filter it off);
- (2) temperature (the higher the temperature of a solution, the easier is filtration);
- (3) pressure (the higher the pressure, the more rapidly a liquid is filtered off);
- (4) the size of the particles of a solid (the larger the particles of a substance in comparison with the filter pores, the easier is filtration).

The mostly commonly used filters in the laboratory are filter paper, cloth, porous glass, asbestos, etc. It should be taken into

account that materials which in some way interact with the liquid to be filtered off cannot be used as filters.

FILTRATION AT ATMOSPHERIC PRESSURE

This filtration technique is the simplest and is commonly used. Filtration under atmospheric pressure is a process in which a liq-

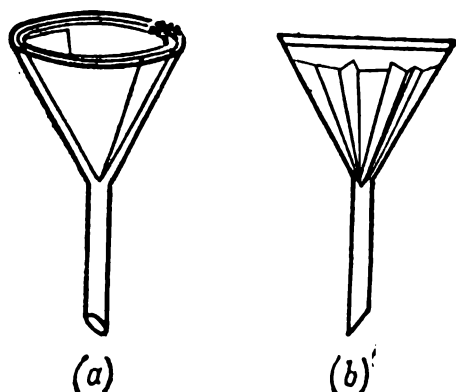


Fig. 2.15. Glass funnels with filters:

a—simple filter; *b*—fluted filter

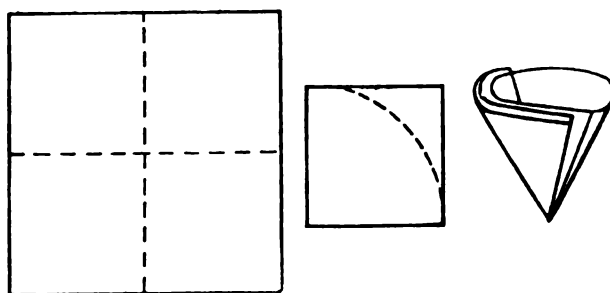


Fig. 2.16. Folding a simple filter

uid passes through a filtering material only under the pressure of the column of the liquid being filtered.

Simple or fluted filters made of filter paper are put into an ordinary glass funnel (Fig. 2.15). To make a simple filter (Fig. 2.16), a square piece of filter paper is folded in quarters and

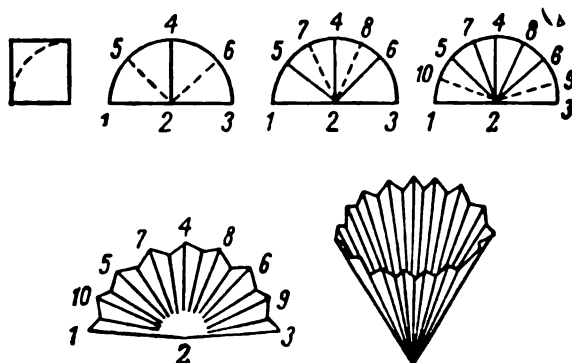


Fig. 2.17. Folding a fluted filter

the free corner of the square formed is cut off with scissors along the dotted line. After removing one sheet of paper from it, straighten out the filter formed so that it becomes cone-shaped.

Filtration is considerably accelerated when a fluted filter is used because its filtering surface is larger than that of a simple filter. The fluted filter is used only when a small amount of a precipitate remains or it can be discarded.

To make a fluted filter (Fig. 2.17), first fold the filter paper in quarters, as in the previous case, and cut off the corner so that the filter is round. The round filter is folded in half and then in quarters; the fold 2-1 is put on 2-4, and the fold 2-3, on 2-4. Then, there are new folds: 2-5 and 2-6. The folds 2-3 and 2-1 are put on the folds 2-5 and 2-6, respectively, obtaining new folds 2-7 and 2-8. The folds 2-10 and 2-9 are similarly obtained. Fold the half-circle in accordion-like folds, thus obtaining a fluted filter after it is opened.

The filter should be so selected that its size is commensurate with the amount of the precipitate. In this case, the edge of the filter in the funnel should always be lower than the edge of the funnel by 3-5 mm. The filter should be as close as possible to the funnel sides, and when it is being adjusted, it should be seen to that its top does not tear. Before filtration, the filter should be wetted by a pure solvent in a funnel. The level of the liquid to be filtered in the funnel should be lower than the paper edge.

If filtration is to be carried out rapidly, the liquid should be in the funnel stem. To this end, a solvent is poured into the funnel above the filter edge to wet the filter, and then the filter is slightly raised and rapidly lowered. A liquid column is thus formed in the

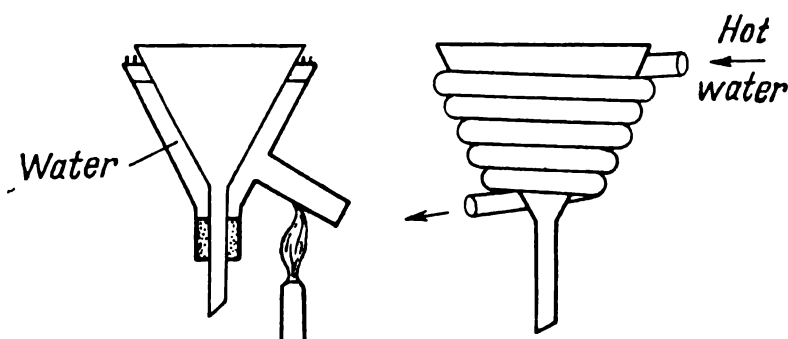


Fig. 2.18. Short-stem conical funnels for filtering hot solutions

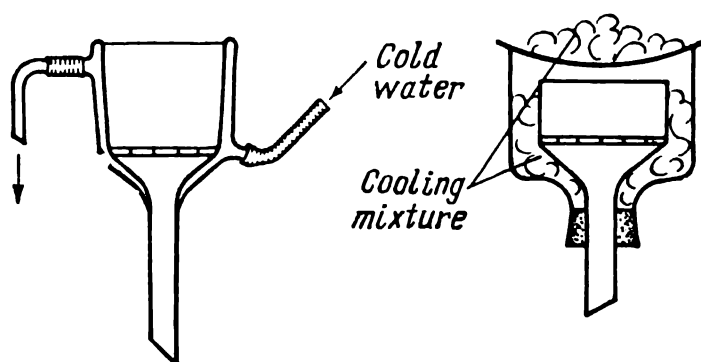


Fig. 2.19. Funnels with a cooling system for filtration

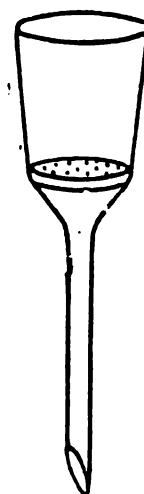


Fig. 2.20. Funnel with a fritted disc

stem. Filtration is carried out with heating when a liquid is very viscous and when recrystallization is being performed (see p. 59). Short-stem conical funnels (Fig. 2.18) are usually used for filtering hot solutions in recrystallization. Special funnels with a cooling system (Fig. 2.19) are used for filtering substances which have a low melting point (e.g., acetic acid and benzene). The precipitates are filtered through fritted discs (Fig. 2.20) when there are strong alkalies and acids, anhydrides, oxidizing agents and other substances which destroy filter paper.

SUCTION FILTRATION

In suction filtration, reduced pressure is created in the receiver, as a result of which the liquid is filtered under atmospheric pressure. This accelerates filtration.

The suction apparatus consists of a porcelain Büchner funnel, a Bunsen flask, a trap and a water pump (Fig. 2.21).

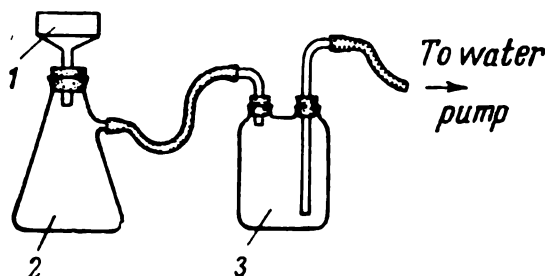


Fig. 2.21. Suction apparatus:
1—Büchner funnel; 2—Bunsen flask; 3—trap

The size of the Büchner funnel should correspond to the amount of the substance to be filtered, i.e., the crystals should completely cover the filter surface, but suction and washing are hampered if their layer is too thick. A trap is put between the Bunsen flask and the vacuum pump and is used to prevent water from being sucked back from the pump to the Bunsen flask; suck-back occurs when water-line pressure decreases suddenly.

The trap is connected to the water pump by heavy-walled rubber tubing, whose sides do not compress when there is rarefaction in the tube.

Water suction pumps, which operate according to the principle of entraining gas particles by a liquid jet (Fig. 2.22), are used most frequently in the chemical laboratory. They are made of either glass or metal. The pumps are attached to the water faucet by a headpiece (Fig. 2.23).

Heavy-walled rubber tubing or a rubberized hose 10 cm long is put on the upper end of the pump; the former is secured by soft iron wire to prevent water from escaping. The other end of

the tubing or the hose is connected by means of a headpiece to the faucet and also tightened by wire. The pump is then checked. For this purpose, the water faucet is opened, while closing the aperture of the side arm of the pump with a finger. If the finger sticks by suction, the pump can be used. Heavy-walled rubber tubing is put on the side arm of the water pump and connected to a trap.

A Büchner funnel is inserted into a flask on a rubber stopper (it is inexpedient to use cork stoppers owing to their porosity). A filter-paper disc, whose diameter is smaller than the inner diameter of the funnel by 1 mm, is put on the bottom of the funnel, covering all the holes. To cut such a disc, a sheet of filter paper

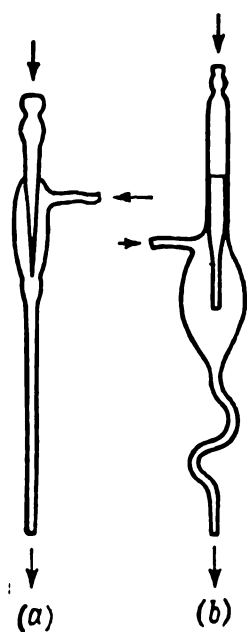


Fig. 2.22. Water suction pumps:
a, b—glass; c—metallic

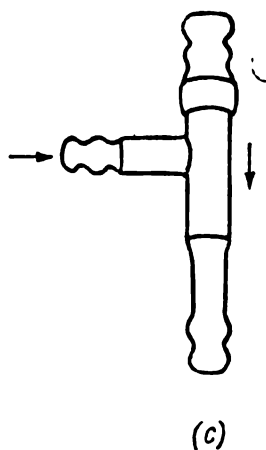


Fig. 2.23. Headpiece for
the water faucet to fas-
ten the water suction
pump

folded half is put on the funnel and slightly pressured with the palm. The paper thus has an impress of the disc of the upper diameter; the disc is then cut with scissors to the required size. After the paper filter is put into the funnel, it is wetted with a solvent and the pump is switched on so that the filter will stick by suction to the bottom of the funnel. There is a smooth noisy sound if the filter is put properly, and a hissing sound if it is not close enough to the wall and air leaks in. After checking the filter, pour the mixture to be filtered into the funnel to one-half its height without switching off the pump.

In filtration, it must be seen to that cracks are not formed on the precipitate surface. This causes irregular, incomplete suction and contaminates the precipitate as a result of solvent evaporation. Moreover, too much filtrate should not collect in the flask; other-

wise, it will be sucked into the pump. The appropriate safety precautions must be taken when filtering flammable liquids. To remove the residues of mother liquor, the crystals are washed on a filter with small amounts of a solvent. To this end, the precipitate on the filter is impregnated with a solvent and the pump is then switched on.

The washed crystals on the filter are pressed by the flat part of a glass stopper until mother liquor no longer drips. The funnel is then taken out, together with the stopper from the flask, and the filter is dumped with the precipitate on filter paper. After scraping the crystals off the paper circle and the funnel walls with a scraper, the product obtained is wrung in filter paper and dried in air or by other techniques (see p. 48).

Chapter 3

METHODS OF PURIFYING ORGANIC SUBSTANCES

3.1. CRYSTALLIZATION

Crystallization is the formation and growth of crystals from a melt, a solution or a gas.

The most important aim of organic synthesis is to obtain pure substances. Organic compounds obtained as a result of one reaction or another are usually "raw" products with impurities. Most solid organic substances are capable of being crystallized and isolated in more or less pure form, when the reaction mixture cools or the solution evaporates. The product obtained must, however, be purified further. Therefore, it is subjected to recrystallization.

Recrystallization is carried out in the following way: a crude substance is dissolved in a hot solvent, the hot solution is passed through a filter to remove suspended insoluble particles, and the solution is cooled; as a result, a substance of greater purity usually crystallizes out of it. But recrystallization causes great losses of a substance in mother liquor. It is therefore expedient to preliminarily purify a product by some other technique, such as simple distillation, steam distillation, or separation from impurities by solvents or surfactants.

An additional amount of a substance can be extracted from mother liquors and wash liquids if a part of the solvent is distilled from them, the solution is cooled, and crystallization is performed. The crystals thus obtained are usually less pure than the initial portion, and they should be recrystallized again.

If a substance was recrystallized from water, mother liquor can be evaporated to one-half its amount in a porcelain dish and then cooled for crystallization.

SOLVENT SELECTION

The correct selection of a solvent is of great importance in recrystallization. When a solvent is being chosen, the chemical properties of the substance to be purified must be taken into account. A substance should dissolve poorly in a selected solvent in the cold and well on heating; the impurities should be either well soluble in a cold solvent or poorly soluble in a hot solvent. In addition, the solvent should not react with the substance being crystallized. It should promote the formation of stable crystals and should be easily removed from the crystal surface in washing and

drying. In selecting a solvent, the principle of *like dissolves like* can often be used. For instance, phenols, carboxylic acids, lower alcohols and other substances containing the hydroxyl group readily dissolve in water; higher esters, in lower ones; higher alcohols, in lower ones, etc. But this principle applies only to substances of simple structure; it is not always valid when complex compounds are involved. The final selection of a solvent can be made only experimentally in test tubes having small amounts of the substance to be purified. In this case, account is taken of the solubility of a substance on heating and in the cold, the crystalline shape of the precipitate, its purity, etc.

A sample of a substance is taken by the end of a spatula and put into a test tube, and a few drops of a solvent are added. If the substance dissolves even in the cold, the given solvent is unsuitable for recrystallization. If a substance either dissolves poorly or does not dissolve at all in the cold, the test tube is carefully heated until the mixture in it boils. A few more drops of the solvent are added whenever necessary so that dissolution will be complete. The hot solution is filtered off. If crystals with the same melting point as that of a pure substance are formed after the solution cools (this is often achieved only in repeated crystallization), then the solvent can be used for crystallization. The constancy of the melting point in repeated crystallization indicates that a solvent can be used for recrystallizing a substance whose melting point is unknown. A given solvent is unsuitable if a substance does not crystallize when a hot saturated solution cools or, conversely, it does not dissolve or dissolves poorly even on heating.

The solvents used in crystallization are water, ethyl and methyl alcohols, benzene, toluene, acetone, ethyl ether, glacial acetic acid, chloroform, ethyl acetate, etc. It is inconvenient to use highly volatile solvents, such as ether and carbon disulphide, because they volatilize too readily from the solution's or the crystal's surface.

When highly flammable solvents (ether, alcohol, acetone, etc.) are being used, dissolution should be carried out very carefully in a flask having a reflux water condenser. Nearby burners and electric heaters with open heating should be turned off.

Mixtures consisting of two and occasionally three solvents are used when an individual solvent cannot be chosen for recrystallization. To this end, dissolve a substance in its quickly dissolving solvent, and add the second hot solvent, which dissolves a given substance poorly, dropwise to the solution obtained until stable turbidity is formed. This mixture is heated to make the solution clear, and then it is allowed to stand for crystallization. The solvents used together should mix with one another in all proportions. In most cases, the following mixtures are used: alcohol-water, al-

cohol-benzene, alcohol-glacial acetic acid, acetone-water, ether-acetone-benzene, and chloroform-petroleum ether.

It is expedient to recrystallize contaminated acetanilide (m.p. 115 °C).

RECRYSTALLIZATION PROCEDURE

To recrystallize a substance, first put it in a flask with a reflux condenser (see Fig. 1.8*b*); this condenser is not needed if the solvent is water. Boiling stones are put into a flask before heating so as not to overheat the liquid and also to preclude bumps when the solution is being boiled. A solvent is then poured into the flask in an amount somewhat less than that needed for the substance to dissolve completely. The mixture is heated until it boils because the solubility curve near the boiling point of a solvent usually sharply rises. If high-boiling solvents are not used, heating is carried out in a water bath. An amount of a solvent that would be enough for completely dissolving the entire substance on boiling is then carefully added through a reflux condenser. Before boiling is resumed, fresh boiling stones should be put after a cold solvent is added because they can no longer be used if the temperature of the solution drops below its boiling point (see p. 36).

A solid crude substance occasionally contains coloured resinous impurities, which are removed with difficulty by recrystallization. In such cases, decolourizing charcoal is added. The amount of charcoal used should not be too much so as to prevent the main product from being adsorbed. Its amount is usually 1-2 per cent of the amount of the substance to be purified. The solution should be somewhat cooled before adding decolourizing charcoal, since charcoal liberates a lot of air, and this can cause the liquid to foam over and be ejected. The mixture is then boiled for 5-10 min with a reflux condenser. The solution is filtered while it is still hot. If the hot saturated solution contains some mechanical impurities or is turbid, filter it as soon as possible through a fluted filter wetted with a solvent on a funnel for hot filtration.

In filtration, a porcelain dish, a conical flask or a beaker can be used as receiver.

If the solution obtained is quite clear and does not contain mechanical impurities, there is no need to carry out filtration because it involves a loss of a certain amount of the substance being crystallized.

FORMATION OF CRYSTALS

When all the mechanical impurities are removed by filtration, the hot clear solution either is left in the vessel covered with a watch glass, allowing it to cool slowly, or is rapidly cooled by

putting the flask in cold water or snow. Small crystals are obtained when the solution is cooled rapidly, and large ones, when it is cooled slowly.

Medium-sized crystals are usually obtained, because large crystals contain inclusions of the mother liquor, while small ones form a dense gruel and mother liquor is also firmly retained between its individual crystals.

Some substances crystallize with great difficulty even when the solution cools. This is due in most cases to very slow crystal growth or very slow nucleation. In the former case, crystallization is carried out for a long time. If nucleation in a solution is slow, nuclei can be created artificially by seeding the solution with some crystals of the same pure substance. Crystallization can be accelerated if the wall of the vessel containing the solution is rubbed with a stirring rod.

In crystallization, low-melting substances tend to separate from solutions in the form of oil. To crystallize such a substance, the solution is diluted with a small amount of a pure solvent, heated until the oil dissolves, and cooled very slowly. Crystallization can be accelerated if the vessel side is rubbed with a stirring rod or seeds are introduced.

Crystallization is complete when crystals are no longer formed. Crystals are separated from mother liquor by suction filtration on the Büchner funnel (see Fig. 2.21) under reduced pressure. After suction, the water pump is switched off. The crystals are covered with a small amount of a solvent and mixed with a stirring rod. Then the water pump is switched on again and the solution is sucked off. Washing the crystals twice with a cold solvent is usually sufficient. After suction and washing, the precipitate is wrung on a funnel by a broad glass stopper, and then it is put on filter paper and dried, in accordance with the properties of a substance, either in air, covering the crystals with another piece of filter paper, or by one of the methods described earlier.

Hygroscopic substances are dried in desiccators, and substances resistant to the action of air and temperature, in drying chambers whose temperature should be 20-50 °C below the melting point of a given substance.

The purity of a substance obtained in crystallization is determined by its melting point after it is dried. If the substance melts at a lower temperature than that indicated in a handbook, repeat crystallization until a substance with the given melting point is obtained. It should be taken into account that the amount of a substance decreases with every recrystallization, because crystallization inevitably involves losses, no matter how carefully it is performed.

3.2. SUBLIMATION

Sublimation is the volatilization of a solid with the subsequent condensation of vapour into a solid state without passing through the liquid phase. This technique is used for purifying solids which have sufficiently high vapour pressure at rather low temperatures. Sublimation is used especially when a solid organic substance cannot be rid of resinous impurities by crystallization. In most cases, sublimation is a rather slow process. The sublimation rate is directly proportional to the vapour pressure of a substance at a certain temperature, and inversely proportional to the external pressure of the device. The smaller the difference between external pressure and the vapour pressure of a substance, the higher the sublimation rate. Moreover, the sublimation rate is directly proportional to the size of the surface of the substance being volatilized, and therefore the substance should be finely ground.

Substances with rather high vapour pressure can acquire, on heating, vapour pressure equal to atmospheric pressure at temperatures below their melting points. The melting point is not reached when these substances are heated because they directly pass over to the vapour state, i.e., they sublime.

The sublimation point (or sublimation temperature) is the temperature at which the vapour pressure above a solid is equal to the external pressure.

Sublimation is carried out both under atmospheric pressure and in a vacuum. To sublime a substance under atmospheric pressure, it is put in a small porcelain dish and covered with a piece of filter paper which has an opening (so that the sublimate would not fall back on the sublimand). Then the porcelain dish is covered with an overturned glass funnel (Fig. 3.1a). The stem of the funnel is closed with a glass-wool wad. The dish containing the substance is heated on a low burner flame or in a sand bath. For cooling, some moistened cotton or cloth is put on the external surface of the funnel. The dish with the substance should be heated carefully because the sublimand can rapidly decompose thermally if it is slightly overheated. It is expedient to use the foregoing technique for subliming benzoic acid or naphthalene.

In vacuum sublimation (Fig. 3.1b), the solids which melt under atmospheric pressure can have a sublimation point below their melting point if pressure is reduced.

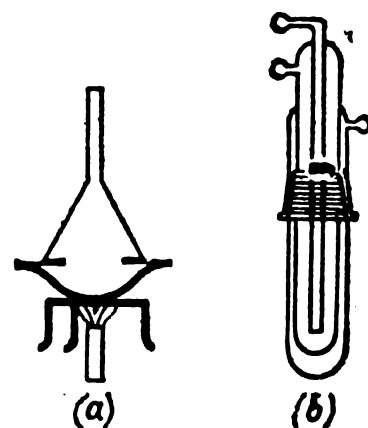


Fig. 3.1. Sublimation apparatus:

a—under atmospheric pressure; *b*—under vacuum

It is expedient to use vacuum sublimation for purifying benzoic acid, oxalic acid (crystal hydrate) and alizarin.

One gram of benzoic or oxalic acid, or an alizarin sample taken on the tip of a spatula, is put in a vacuum sublimation apparatus. When the apparatus is being assembled, the ground-glass joint should be well lubricated. The water cooler is then switched on. When a vacuum is created by an oil pump, the apparatus is slowly heated in a paraffin bath. The temperature of the bath must be controlled. The temperature at which sublimation begins should be recorded in a laboratory notebook. When sublimation is completed, the apparatus is allowed to cool and then carefully opened. If the ground-glass joint cannot be opened, a glass blower should be consulted.

3.3. EXTRACTION

The extraction method is often used for removing impurities from substances and separating substances from a mixture. A substance can be extracted both from a mixture of solids and from solutions, depending on whether it is a solid or a liquid.

A very important operation in the laboratory of organic chemistry is the extraction of substances from solutions (mostly from aqueous ones). In this operation, a solution in a definite solvent (usually water) is shaken with another solvent which does not mix with the initial one.

To extract organic compounds from aqueous solutions, use is often made of diethyl and petroleum ethers, gasoline, benzene, chloroform, etc. In this case, it is necessary to select a solvent in which the substance to be extracted dissolves best of all, or which is the easiest to remove from the extract. Substances which dissolve poorly in water should practically be extracted from the aqueous solution by petroleum ether or gasoline, while those which dissolve well in water, by ether, which has a low boiling point and a great ability to dissolve organic compounds. All the nearby burners should be turned off when flammable solvents are being used.

Substances are extracted from aqueous solutions and immiscible liquids are separated by separatory funnels of different shapes (Fig. 3.2). Before commencing work, the ground-glass stopper at the top and the stopcock at the bottom of the separatory funnel are lubricated with Vaseline. The lubricant should not be put on thickly because it can pass into the solution if it comes into contact with ether. The solution is then poured into the separatory funnel and a solvent is added (from one-fifth to one-third of the amount of solution); be sure that the amount of the liquid in the funnel is not greater than two-thirds of its volume. The separatory funnel is closed with a stopper and carefully shaken, smoothly turning it up and down for 5-15 min while holding the stopper in one hand, and the stopcock in the other. The contents of the funnel should by no

means be vigorously shaken because stable emulsions which are difficult to decompose are then formed.

The pressure in the funnel usually rises when it is shaken (a part of the solution turns into vapour). To equalize the pressure after the funnel is carefully shaken for a short time, the stopcock is opened while the funnel is held upside down. Ether vapours which have accumulated are discharged through the open stopcock, and pressure is equalized with atmospheric pressure. The stopcock is then closed and the content of the funnel is slowly shaken again. Afterwards, the stopcock is reopened. This is done several times. After shaking, the separatory funnel is clamped on a ring stand and the liquid is allowed to completely separate into two layers. Both layers (ethereal and water) should be clear. The stopper is then taken out and the stopcock carefully turned, allowing the lower layer to flow out slowly into a vessel. See to it that a part of the upper layer is not poured off together with the lower one. The upper layer is always poured out through the upper opening of the separatory funnel into a receiver.

The organic products of a reaction usually pass to the upper ethereal layer, while inorganic salts, acids and bases, to the water layer. In dubious cases, however, when the water layer must be ascertained, several drops of a layer are taken and added to a test tube containing water. If the drops do not dissolve, the layer from which they have been taken is an ethereal one.

To extract a substance as thoroughly as possible, the water layer is put again into the separatory funnel and the substance is extracted by another portion of ether, performing the same operations as before. Substances which dissolve poorly in water are extracted with two portions of a solvent, while compounds which dissolve well in water are extracted about four times. In extraction, it is more expedient to extract a substance several times by small portions of a solvent than to immediately treat a solution with a large amount of a solvent.

The best extraction conditions are determined on the basis of Nernst's distribution law, according to which the ratio of the concentrations of a substance dissolved in two immiscible solvents which are in equilibrium (e.g., in water and ether) is a constant at a given temperature:

$$K = \frac{C_A}{C_B}$$

where K = distribution coefficient;

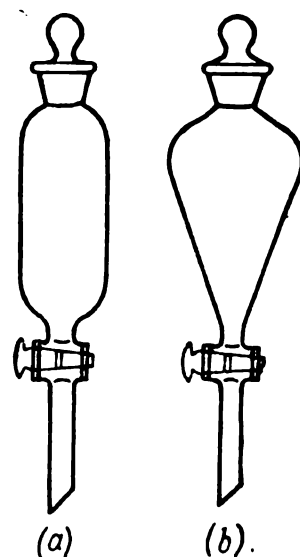


Fig. 3.2. Separatory funnels:
a—cylindrical; b—conical

C_A and C_B = concentrations of a substance dissolved in both solvents.

A substance can be easily extracted if it dissolves in the extractant far more readily than in another solvent, and the distribution coefficient consequently considerably differs from unity. It is not enough to extract a substance once if its distribution coefficient K is less than 100. In this case, extraction is repeated many times with a fresh solvent.

Combined ethereal extracts are usually cleansed of impurities, in most cases acids or bases entrained with the solvent in extraction. To this end, they are washed, i.e., they are shaken once or twice in a separatory funnel with a dilute aqueous solution of alkali (soda or sodium bicarbonate) or acid and, in conclusion, washed once or twice with water. In this case, it should always be borne in mind that carbon dioxide can be liberated and pressure in the separatory funnel can rise when the extract is being washed with soda. Therefore the gas being liberated should be carefully let out through the stopcock, if it is on the top.

The extract is then dried with a suitable drying agent (see p. 48). After drying, the extract is decanted or filtered through a fluted filter. The ether is removed by driving it off in a water bath (see p. 45), while the residue is purified by crystallization, sublimation or distillation.

Sparingly separable emulsions are often formed in extraction from liquids, especially from aqueous solutions. Mixtures which tend to form emulsions are not shaken vigorously, but only slightly, in a separatory funnel. Emulsions are formed for different reasons. One reason is that there is a negligible amount of a light precipitate which is collected at the interface. Another reason is that surface tension at the liquid-liquid interface is high and the densities of the two liquids differ only slightly.

Various methods are used to destroy an emulsion, depending on the reasons of its formation. An emulsion being formed can be destroyed by adding several drops of ethyl alcohol, which reduces surface tension, by filtering the solution by suction (see Fig. 2.21), by allowing the solution to stand for a long time, or by saturating it with common salt so as to increase the density of the water layer.

In many cases when a substance is being extracted from an aqueous solution, it is expedient to saturate the solution beforehand by some inorganic salt, such as common salt or ammonium sulphate. The solubility of most organic compounds in water then diminishes and, at the same time, less solvent is lost because the solubility of the latter in water also diminishes. Solutions are continuously extracted when the substance to be extracted dissolves

better in water than in organic solvents and extraction in a separatory funnel does not produce good results.

Figure 3.3 shows a very simple apparatus which can be employed when small amounts of a solution are used. A solvent in a round-bottom flask is heated in a water bath until it boils. Its vapours pass through the vapour outlet tube into the reflux condenser, where they are condensed. The condensate drips into the funnel which is inserted into a wide test tube containing the liquid

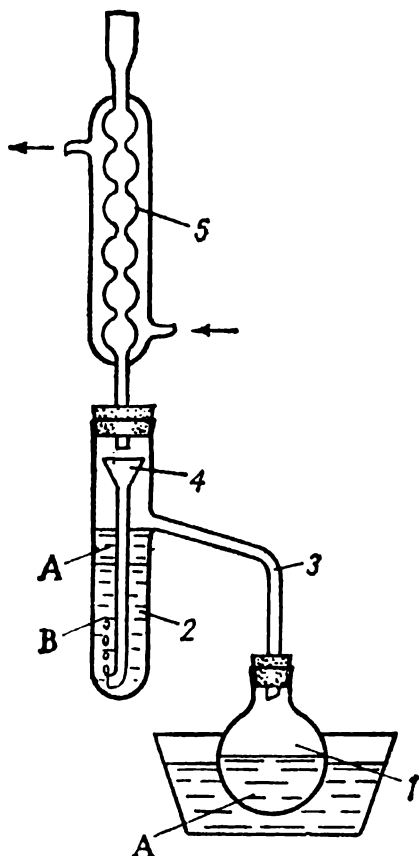


Fig. 3.3. Apparatus for multiple extraction of solutions:

1—round-bottom flask; 2—test tube; 3—vapour outlet tube; 4—funnel; 5—reflux condenser; A—solvent; B—solution to be extracted

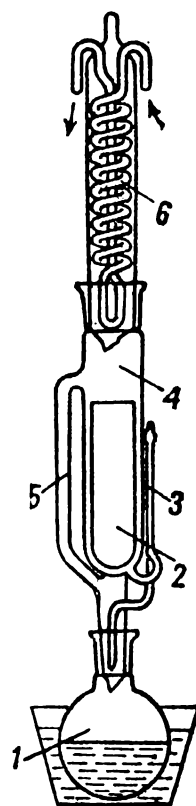


Fig. 3.4. Soxhlet apparatus:

1—round-bottom flask; 2—cartridge; 3—extract drainage tube; 4—extractor; 5—vapour outlet tube; 6—reflux condenser

to be extracted. Since the density of the liquid is greater than that of the solvent, the latter, while flowing out of the funnel, passes through the layer of the solution to be extracted, extracts the substance dissolved in it, rises to the solution surface and drips back into the flask.

Solids often must be extracted in the laboratory. Soxhlet apparatus (it is best if they have ground-glass joints, Fig. 3.4) are used to this end. The Soxhlet apparatus consists of a round-bottom flask, an extractor and a reflux condenser. The solvent-containing flask is connected to the extractor, which contains the substance to be extracted tightly wrapped in filter paper or put in

a special cartridge. The solvent in the flask is heated in a water bath until it boils. Its vapours pass through the vapour outlet tube into the extractor and then into the condenser, where they are condensed. The condensate drips into the cartridge containing the substance to be extracted, extracts the necessary compound and flows back into the flask through the extract outlet tube. In this case, the extracted substance gradually accumulates in the flask, while the amount of the liquid practically does not change. Therefore, a limited amount of a solvent can be used to extract an unlimited amount of a substance, because it is always treated with a pure solvent. After completing extraction, the water is turned off, the condenser is taken off, the extractor is removed, the residues of the liquid are allowed to drip from it into the flask, and then the solvent is driven off.

3.4. DISTILLATION

One of the most important methods of purifying and isolating organic substances is distillation, which is the separation of a liquid mixture by heating a liquid until it boils and condensing its vapours as a distillate in a condenser.

Whenever a liquid evaporates, it has definite vapour pressure, since over it exists an equilibrium between it and the vapour. The quantity of this pressure depends on the nature of the liquid and the temperature. Vapour pressure over a liquid greatly increases with an elevation of temperature.

The temperature at which vapour pressure becomes equal to atmospheric pressure is called the boiling point. Any liquid which does not decompose when it is heated to a temperature at which vapour pressure is equal to 760 mm Hg has its own characteristic boiling point under atmospheric pressure.

Since the boiling point greatly depends on pressure, it is always necessary to indicate the pressure at which the boiling point has been observed. If the pressure is not indicated, the temperature has been determined under atmospheric pressure.

The boiling point can be affected differently by impurities in a substance, and therefore is less suitable for identifying liquids and characterizing their frequencies than the melting points of solids.

SIMPLE DISTILLATION AT ATMOSPHERIC PRESSURE

When the substance to be distilled is sufficiently resistant to heating and practically does not decompose at the boiling point, simple distillation at atmospheric pressure is used for purification. It is expedient to use this distillation technique usually for liquids

whose boiling point is in the 40-150 °C range because many substances noticeably decompose above 150 °C, while the distillation of liquids with a boiling point below 40 °C entails substantial losses. In distillation, the temperature of a boiling liquid is often somewhat higher than that of vapour due to superheating. Superheatings, which originate because there are no boiling centres in the liquid being distilled, cause strong bumps, as a result of which a substance together with impurities can be ejected into the receiver. There are various techniques for preventing or weakening the bumps when a liquid boils. In most cases, boiling stones are put in a flask containing the liquid to be distilled.

Before a substance is isolated by distillation, it is often necessary to heat a mixture of reagents for many hours at the boiling point in order to allow them to react with one another. In such cases, a liquid is boiled in a device which has a reflux condenser. If a reaction is to be carried out while simultaneously introducing a liquid to a flask and stirring the mixture, use a three-necked flask or two or three-mouth adapters (Fig. 3.5).

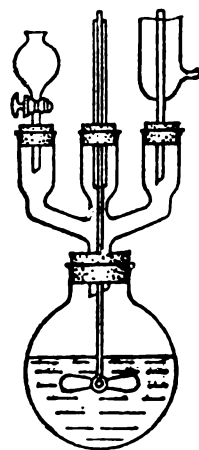


Fig. 3.5. Apparatus for boiling a mixture while simultaneously introducing a liquid and stirring

Round-bottom flasks, mainly the Würtz flasks, are usually used as distilling vessels. To distil low-boiling liquids, use the Würtz flask with an outlet tube sealed high on it. The same flask with the outlet tube sealed low on it is used to distil high-boiling liquids. The boiling point is usually controlled by a thermometer whose mercury bulb should be completely covered by a boiling substance's vapours, i.e., the upper end of the bulb should be about 0.5 cm lower than the opening of the flask's outlet tube. Occasionally, the vapour temperature does not have to be strictly controlled in distillation; in such cases, either the neck of the Würtz flask is closed with a stopper without a thermometer or use is made of a round-bottom flask which is connected to the condenser by a bend glass tube.

The volume of the distilling flask is selected in conformity with the amount of liquid to be distilled and its boiling point. The liquid should occupy no more than two-thirds of the volume of the flask; otherwise, it can be ejected into the receiver when it is being boiled. The flask should not be too large, especially when high-boiling liquids are to be distilled because a large amount of the substance being distilled remains in it.

The flask is secured in a support by gripping it with a clamp above the outlet tube. To prevent a substance from being con-

taminated, the distillate should, whenever possible, not come into contact with the stoppers, and therefore the outlet tube of the distillation flask is so connected to the condenser that its end extends from the stopper into the condenser by at least 4-5 cm and reaches the part of the condenser that is cooled by water. The size of the condenser is selected in conformity with the distillation rate and the boiling point of the liquid to be distilled. Details on condensers are given on page 20.

The vapours of substances which readily crystallize at room temperature should not be cooled in a condenser to the solidification point. To this end, the condenser can be intermittently heated by a jet of warm water.

Liquids which boil within the 200-300 °C range are distilled without a condenser, whose function can be performed in this case by the outlet tube of the Würtz flask.

To reduce, whenever possible, the losses of a substance as a result of the evaporation of the distillate in the receiver, it is connected to the adapter of a condenser by means of a bent adapter. A conical or round-bottom flask is usually used as a receiver. To condense the vapours of low-boiling liquids more thoroughly, the receiver is put into a vessel containing the mixture being cooled.

Heating is commenced only when the entire apparatus is assembled and has been thoroughly checked. Heating is carried out by a gas burner through an asbestos net, on a closed electric heater or in a bath (p. 34), depending on the boiling point. The distillation rate selected is usually such that not more than 1-2 drops of the distillate drip per second. The low-boiling solvent must often be distilled off at first in many operations. This should be done in a water bath because most solvents are flammable (see Chap. 1) and a substance does not have to be subjected to thermal action once more if there is no need. After the solvent is driven off, a few boiling stones are put into the cooled flask and the substance is distilled off as usual.

STEAM DISTILLATION

Steam distillation is one of the commonly used methods of separating and purifying organic substances. This method is widely used not only in the laboratory, but also in industry. Steam distillation is applied to substances which practically do not mix with water and do not chemically interact with it.

Steam distillation is carried out in the following cases:

1. To separate a substance from a mixture and purify many substances which either boil at very high temperatures or cannot be distilled off at all without decomposition.

2. To purify substances which are contaminated by a large amount of resinous impurities.

3. To separate mixtures of substances, only one substance of which is distilled off with steam (for instance, natural resins and oils can be separated by this method into steam-volatile and non-volatile fractions).

4. To separate solids which do not volatilize with steam from their solutions in solvents which have a high boiling point (such as nitrobenzene with a boiling point of 210°C, which is distilled off with steam at 99°C).

5. To separate sparingly water-soluble substances which have noticeable vapour pressure at about 100°C.

As temperature rises, steam pressure and the pressure of vapours of a water-immiscible substance increase practically irrespective of one another.

Boiling begins when the sum of partial pressures of saturated vapour is equal to atmospheric pressure. Therefore, according to Dalton's law, total vapour pressure P is the sum of the partial pressures of the vapours of the substance being distilled off A and water B: $P = P_A + P_B$. Thus, this mixture is distilled off at a lower temperature than pure water. The distillate has the vapours of water as well as those of the substance being distilled.

The relative amount of a substance being distilled off with steam can be found by the following equation:

$$\frac{Q_A}{Q_B} = \frac{P_A M_A}{P_B M_B}$$

where Q_A = amount of a substance in the distillate;

Q_B = amount of water in the distillate;

M_A = molecular weight of a substance;

M_B = molecular weight of water;

P_A = pressure of vapours of a substance at the distillation temperature;

P_B = pressure of water vapours at the distillation temperature.

The pressure of water vapours P_B at the distillation temperature can be found for every case in Supplement 2. The pressure of vapours of a substance P_A is consequently equal to $760 - P_B$.

Hence, the weight of water needed for distilling off one gram of a substance can be determined:

$$Q_B = \frac{P_B M_B}{M_A (760 - P_B)}$$

For instance, a mixture of nitrobenzene (b.p. 210°C) and water is distilled off at 99°C.

Using Supplement 2, we find

$$\frac{733 \times 18}{123 \times 27} = 4$$

i.e., 4 g of water are needed for distilling off one gram of nitrobenzene.

Steam distillation is carried out in an apparatus (Fig. 3.6) consisting of a steam generator, a distilling flask, a condenser and a receiver.

The generator (boiler) is a metallic vessel (it can be replaced by an ordinary round-bottom 1.5-2 litre flask) which has a safety tube and a water-gauge tube. The safety tube almost reaches the bottom of the steam generator and protects the system from a sharp rise in pressure caused by intensive heating. When pressure increases, water usually rises along the tube, and occasionally it is

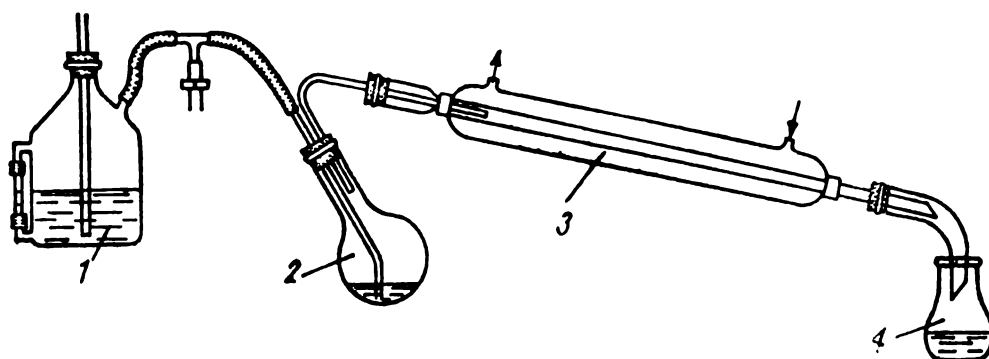


Fig. 3.6. Steam distillation apparatus:

1—steam generator; 2—distilling flask; 3—condenser; 4—receiver

even ejected outside. In such cases, the flame should be reduced.

The steam generator is connected to the distilling flask by a rubber tube. The Würtz flask (with a tube sealed high) or an ordinary round-bottom flask can be used as a distilling flask. The tube along which steam enters the flask should almost reach the bottom of the flask. The liquid being distilled must not be ejected into the receiver. Therefore, a special long-neck flask is placed in an inclined position to prevent the liquid from passing into the vapour outlet tube which protrudes only slightly from the stopper. The other end of the tube is connected to the condenser. The flask is filled with a liquid whose amount is not more than one-third of its volume. A glass T-piece is placed between the steam generator and the flask, and a rubber tube with a screw clamp is put on its side arm. The T-piece makes it possible to dismantle the apparatus when the flask and the steam generator cool; moreover, it acts as a water separator. The fact is that vapour from the generator is moist, and the distilling flask can be rapidly filled up with water. Water is accumulated in the side arm of the T-piece and is let out every now and then.

Steam distillation is carried out in the following way: a steam generator is filled with water to about two-thirds of its volume and heated to the boiling point. The distilling flask is heated simultaneously. During this time, the rubber tube on the T-piece is open.

The distilling flask should be preliminarily heated; otherwise, steam entering the flask will cool and condense, increasing the liquid volume. The liquid volume will be almost unchanged if the mixture is heated beforehand.

When water in the steam generator boils, the rubber tube is closed and distillation is commenced. The vapours formed condense in the condenser and enter the receiver as an emulsion.

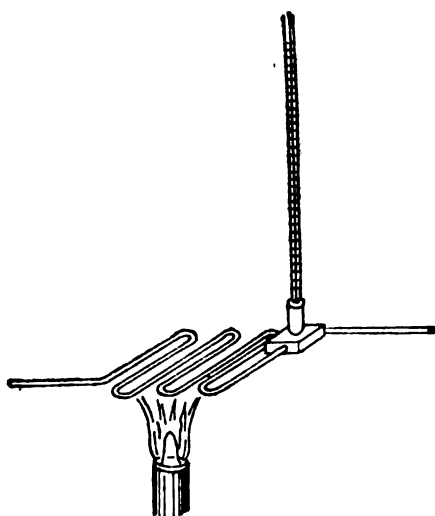


Fig. 3.7. Superheater with a thermometer

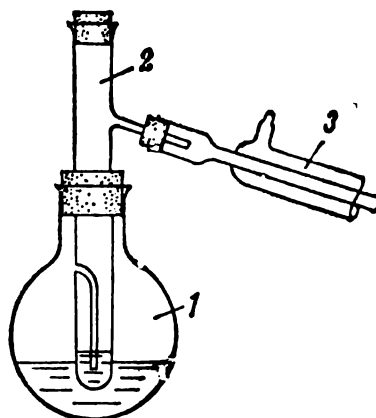


Fig. 3.8. Apparatus for distilling small amounts of substances with steam:

1—round-bottom flask; 2—test tube with two branches; 3—condenser

If a substance precipitates as crystals in a condenser, the supply of cooling water is briefly stopped and the vapours of the substance that come from the flask melt the crystals. It must be seen to it that the vapours which have not condensed do not entrain the substance being distilled. Care should be taken when letting cold water into the condenser.

Distillation is carried out until clear water runs out of the condenser. After completing distillation, first the clamp is opened and then the burners are turned off; otherwise, when the steam generator cools, a vacuum is created in it and the liquid can be sucked from the distilling flask into the boiler.

The distillate is separated in a separatory funnel, and then the last bit of a substance is extracted from water by a solvent (see p. 65).

To increase the yield of the substance being distilled, it is expedient to add sodium chloride to water when the density of a

given substance is similar to that of water. This addition reduces the solubility of an organic substance in water and promotes separation, since the density of an aqueous solution increases.

Superheated steam, which is obtained in superheaters (Fig. 3.7), can be used for distilling substances whose vapours have a pressure which is so insignificant at 100 °C that they are very poorly distilled off with steam. The superheater used is a spiral copper tube put between the steam generator and the distilling flask. It is heated by a burner to the necessary temperature. The distilling flask is put in an oil bath heated to a temperature about 10 °C higher than the temperature of the superheated vapour being supplied. Small amounts of a substance can be distilled with steam in an apparatus shown in Fig. 3.8.

VACUUM DISTILLATION (AT REDUCED PRESSURE)

When pressure drops, the boiling point of a liquid decreases. This property is used very often both in the laboratory and in industry. Some substances decompose when they are heated to the boiling point under atmospheric pressure. Therefore, distillation under reduced pressure (in a vacuum) is used for purifying such substances. Distillation is usually carried out when residual pressure is from 50 to 1 mm Hg. In some cases, a pressure of less than 1 mm Hg is used, such as in high-vacuum and molecular distillation.

There is a considerably greater decrease in the boiling point when pressure drops in the low-pressure region. When atmospheric pressure is reduced by 10 mm Hg, the boiling point of a liquid decreases by less than 1 °C. When external pressure is halved, the boiling point decreases by about 15 °C. For instance, a substance under atmospheric pressure (760 mm Hg) boils at 180 °C; when the pressure is 380 mm Hg, it boils at about 165 °C, and 190 mm Hg, at approximately 150 °C.

The vacuum distillation apparatus (Fig. 3.9) consists of the Claisen flask (with a capillary tube and a thermometer), a condenser, a receiver, a manometer, a T-piece, a trap and a water or oil pump. It is better to use apparatus having ground joints, which protect a distillate from contamination. If a laboratory does not have such apparatus, use should be made of rubber stoppers and heavy-walled rubber tubes. Rubber stoppers should enter the opening of an apparatus by one-third to one-half of their length. It is very useful to slightly lubricate the stoppers with glycerol, but only so that the surface of the stopper does not have a greasy luster. A disadvantage of rubber stoppers is that they are capable of readily absorbing the vapours of many organic substances, as a result of which they swell and crack. Sometimes, use can be

made of cork stoppers impregnated with a solution of liquid glass or paraffin (see Chap. 1).

Before using rubber tubes intended for vacuum distillation, they should be cleaned by boiling in a dilute solution of sodium hydroxide or acetic acid for 10 min, and then thoroughly washed with a water jet and dried by blowing or sucking air through them. It is expedient to keep the processed rubber tubes away from solvents and oils. Before a thick-walled rubber tube is put on a fire-polished glass tube, the surface of the latter must be thinly lubricated with glycerol.

The Claisen flask is immersed in a bath. This ensures uniform heating. The temperature of the bath should be about 20-30°C higher than the boiling point of the substance. The flask is so immersed in the bath that the level of the liquid to be distilled is

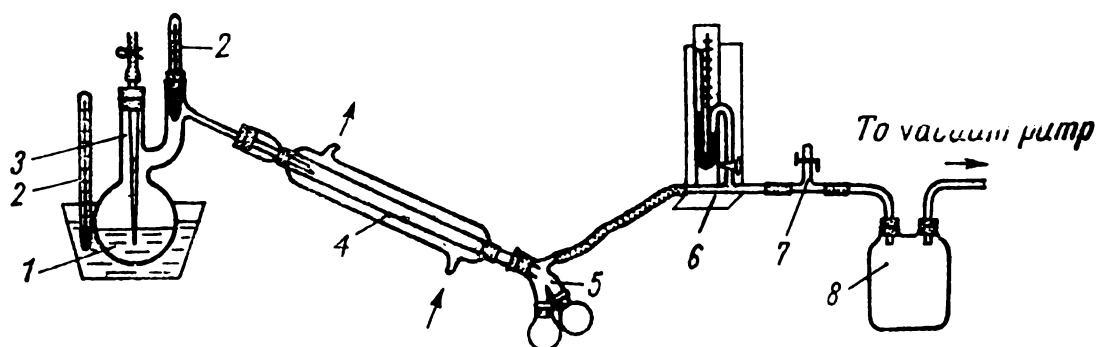


Fig. 3.9. Vacuum distillation apparatus:

1—Claisen flask; 2—thermometers; 3—capillary tube; 4—condenser; 5—receiver; 6—manometer; 7—T-piece; 8—trap

slightly lower than that of the liquid in the bath. The Claisen flask is so shaped that the possibility of the splashing of the liquid being distilled into the distillate on frothing or splashing is reduced to a minimum. When a two-neck Claisen flask is used, a thermometer and a capillary tube can be fitted in the necks of the flask by rubber tubes. If contact between the vapours of a substance and rubber is to be avoided, use the Claisen flasks whose necks are drawn out at the ends. In such flasks, the thermometer and the capillary tube are fastened by short rubber tubes, which are put on the necks (Fig. 3.10).

To maintain uniform boiling, a glass tube terminating in a thin capillary is put into the flask so that it almost reaches the bottom of the flask (1-2 mm from the bottom). Minute air bubbles are continuously sucked through this capillary tube (if the substance reacts with oxygen, it is necessary to pass through argon, nitrogen or carbon dioxide). The amount of air which enters through the capillary tube into the flask can be controlled by a screw clamp put on a thick-walled rubber tube which is fitted on the capillary tube. It is expedient to put a thread or a thin wire

into the rubber tube so that the cross section of the tube will not be completely closed.

The capillary tube is made of glass tubing with a diameter of 4-8 mm. The tubing is at first elongated in a burner flame into a rather thin capillary tube, which is heated again, drawing it in a small flame to a thin thread. To see whether the capillary tube has an opening, put it into a test tube with ether and blow air through it. The bubbles should come out slowly one by one, since the vacuum is reduced when large amounts of air pass through the capillary tube.

When volatile substances with a boiling point below 150°C are being distilled, a short water condenser must be connected to the outlet tube of the Claisen flask, because some of the substance being distilled is lost when the distillate vapours are incompletely condensed. Liquids which boil within the $150\text{--}200^{\circ}\text{C}$ range do not require great cooling; it is enough to cool the receiver by a water jet (Fig. 3.11).

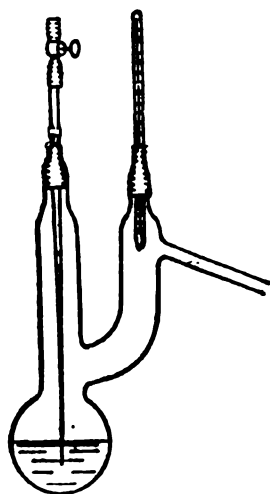


Fig. 3.10. Attachment of the thermometer and the capillary tube in the Claisen flask by rubber bands

The Würtz flasks or heavy-walled vacuum flasks are used as receivers when a substance is being distilled without fractionation. A bent adapter with side arms (Fig. 3.12) is used for collecting several distillate fractions. Test tubes or round-bottom flasks intended for collecting separate fractions are connected to the side arms on rubber stoppers. The upper end of the bent adapter has an outlet tube through

which air is sucked off. To collect fractions in vacuum distillation, the bent adapter is turned around its axis. The stopper should be slightly lubricated with glycerol. To create a vacuum, water pumps or special vacuum pumps, which create great rarefaction, are most frequently used in the laboratory.

The water pump reduces pressure to about 10 mm Hg, depending on the temperature of water. The mercury manometer (Fig. 3.13) is used to measure rarefaction in vacuum distillation; it is connected in the apparatus between the receiver and the trap of the water pump. The trap is connected to the apparatus so as to preclude the suck-back of water from the pump into the manometer or the apparatus (for instance, when the pressure of water in the water supply line suddenly drops). A glass T-piece with screw clamps put on rubber tubes is placed between the manometer and the trap. The T-piece makes it possible to connect the apparatus to the pump or give it access to the atmosphere.

When beginning vacuum distillation, it is necessary to take all safety precautions and *put on safety glasses or plastic safety face screens*.

The success of vacuum distillation largely depends on the correct assembly of an apparatus, attention especially being paid to the tightness of the apparatus. The rubber tubing connected to the capillary tube is tightly closed by a clamp and the pump is turned on. Then see how soon the necessary pressure reaches a value adequate for distillation. When the apparatus is disconnected from the pump by turning off the clamp, the level of mercury in the manometer should remain unchanged. If this test is not passed satis-

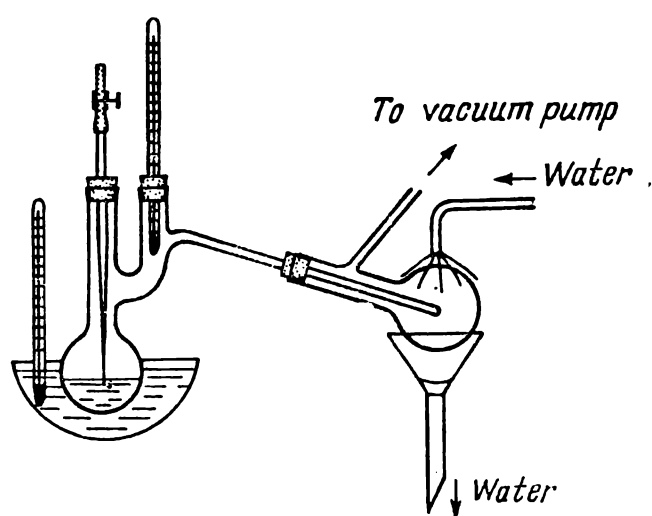


Fig. 3.11. Apparatus for distilling high-boiling substances under vacuum

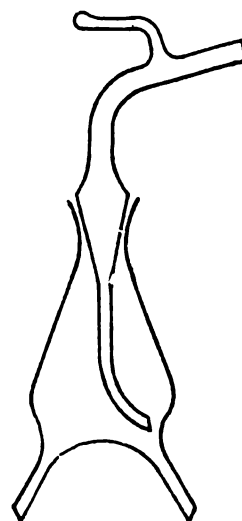


Fig. 3.12. Bent adapter with side arms

factorily, all the joints are checked, the stoppers are inserted more tightly, the rubber tubes are put on more deeply, etc.

After checking the apparatus for tightness, the Claisen flask is filled with the liquid to be distilled to one-half of its volume through the neck intended for the thermometer. The pump is then turned on and, when the required pressure is created in the apparatus, the flask is gradually heated in a water, oil or Wood's alloy bath. The temperature of the bath, being measured with a thermometer, should be higher than the boiling point of the substance by 20-30°C. The clamp is used to control the inlet of air through the capillary tube so that boiling will be uniform. When the liquid begins to boil, heating is controlled so that no more than two drops will drip per second into the receiver.

The Claisen flask is insulated against loss of heat by asbestos if the vapours of a liquid abundantly condense on its sides and distillation is too slow. If a distilling flask is to be intensely heated during vacuum distillation, the temperature should be elevated gradually to the required limit, because a sharp rise in

temperature will cause rapid vaporization and an air-explosive mixture of vapours of the substance being distilled can be formed.

After completing distillation, it is necessary, first and foremost, to stop heating and then to remove the bath so that the Claisen flask can rapidly cool. Disconnect the apparatus and the manometer from the vacuum pump by turning the clamp, turn off the vacuum pump and, by slowly opening the screw clamp which grips the rubber tubing on the capillary tube of the Claisen flask, allow

air to enter the apparatus so as to equalize pressure. If a very thin capillary tube has been used when the apparatus was being assembled and there is no screw clamp for controlling the inlet of air, air should be let into the apparatus by carefully opening the clamp at the T-piece.

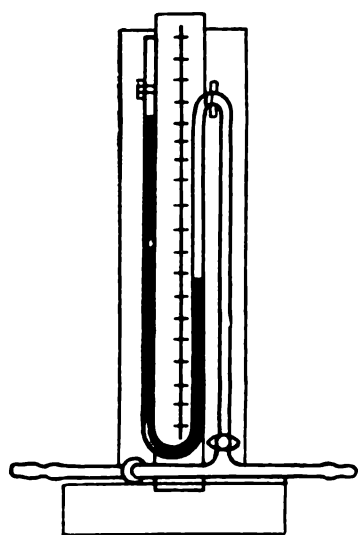


Fig. 3.13. Mercury manometer

The force of air suction is controlled by a manometer; in this case, mercury should slowly pass from the open arm to the closed one. If a lot of air is immediately let in, mercury can make a hole in the closed arm, and the manometer will then be out of order; moreover, liquid residues in the Claisen flask can splash over and contaminate the distillate in the receiver. When pressure in the apparatus becomes equal to atmospheric pressure, the apparatus can be dismantled. First, the receiver is disconnected, and then the Claisen flask. The thermometer and then the capillary tube are carefully taken out of the flask.

FRACTIONAL DISTILLATION

In simple distillation, the content of the low-boiling component in outgoing vapours continuously diminishes as a mixture evaporates (if the mixture consists of two components); they contain the maximum amount of a low-boiling component when distillation begins. In this case, several fractions of a different composition can be obtained by collecting them separately. Distillation with the separation of a mixture into several fractions which are enriched to different extents by a low-boiling component is known as fractional distillation.

The theory of fractional distillation is based on two laws of phase equilibrium in the liquid-vapour system that had been elaborated by D. P. Kononov in 1881-1884.

Konovalov's laws have the following modern formulation:

(1) In a liquid-liquid system, the vapour is relatively richer as a result of the component whose addition increases total vapour pressure.

(2) A liquid mixture whose saturated vapour is of the same composition corresponds to the maximum or minimum of the vapour pressure of a liquid-liquid system.

Two corollaries issue from Konovalov's laws:

(1) In a liquid-liquid system, the vapour is relatively richer as a result of the component whose addition reduces the boiling point.

(2) A liquid and a vapour with the same qualitative and quantitative compositions correspond to the maximum or minimum boiling point of a liquid-liquid system.

Mixtures of infinitely miscible liquids are divided into two classes. The mixtures of the first class can be separated into pure components, and they do not form constant-boiling mixtures. The mixtures of the second class form constant-boiling mixtures, which can never be separated into pure components by distillation, notwithstanding the different boiling points of pure substances.

The mixtures of the first class have vapour pressure which, by its quantity, is intermediate between the pressures of vapours of both pure components (for simplicity's sake, let us consider the distillation of binary mixtures). A low-boiling liquid has high vapour pressure, which becomes equal to atmospheric pressure at a relatively low temperature, while a high-boiling liquid has low vapour pressure, which becomes equal to atmospheric pressure only at a relatively high temperature.

The mixtures of the first class form vapours in which the content of a highly volatile component is always greater than in the initial mixture. Therefore, the liquid in the flask is increasingly enriched by a high-boiling component in distillation.

Dephlegmators (or fractionating columns, see Fig. 1.10) should be used if a mixture is to be separated more effectively and the number of distillations reduced. When they are used, a part of the vapours of the mixture being distilled is condensed as a result of cooling by external air. The condensed vapours, known as the reflux, drip back into the flask, thus becoming enriched by a high-boiling component, while vapours which rise further are enriched by a low-boiling component. The structure of dephlegmators ensures good contact between the liquid which flows down (reflux) and the vapour which rises. There is continuous thermal and material exchange in the counterflow system formed, as a result of which vapour is enriched by a low-boiling component, while the dripping liquid, by a high-boiling component.

The ratio of the quantity of the condensate which returns to the dephlegmator as reflux to the overall quantity of the distillate obtained during the same period of time is known as the reflux ratio. This quantity can be used to determine the effectiveness of the entire process because it characterizes both the precision of separating the mixture into components and the duration of distillation. For instance, in case of a large reflux ratio, the separation of a mixture is all the more thorough when the distillation rate is lower.

Let us consider the separation of a mixture of benzene and toluene by fractional distillation. It is convenient to use this mixture because its components have different boiling points.

To carry out the experiment, use a definite weighed amount of a mixture of toluene (b. p. 110.6°C ; $d = 0.86$) and benzene (b. p. 80.2°C ; $d = 0.88$). When beginning distillation, it is necessary to write down the weights of the flask and the mixture or the overall volume (in ml) in the laboratory notebook.

To carry out fractional distillation, an apparatus consisting of a round-bottom flask, a dephlegmator, a thermometer, a condenser, a bent adapter and a receiver (see Fig. 1.11) is assembled. The round-bottom flask containing the distilland should be no more than two-thirds full. A dephlegmator, being selected with regard to the properties of the liquids which form a mixture, is inserted with the aid of a stopper into the flask which is placed in a sand bath and supported in a ring stand. For instance, a long dephlegmator is used for substances which boil below 150°C , and a short one for substances which boil above 150°C . In our case (benzene + toluene), a long dephlegmator must be used. The dephlegmator is also supported. It is then connected to the condenser, and a stopper with a thermometer is put into it. It should be borne in mind that the Liebig water condenser is used for substances which boil below 150°C , and an air condenser, for substances which boil above 150°C . In this case, the water condenser should be used. The thermometer is so secured that the section of the scale between 75°C and 120°C is not covered by the stopper, while the upper edge of the mercury bulb is about 0.5 cm below the opening discharge tube of the dephlegmator. The mercury bulb should not touch the glass. Afterwards, a bent adapter is attached to the condenser and a receiver is placed underneath. It is necessary to prepare three receivers (flat-bottom flasks) which are preliminarily weighed together with the stoppers by the technical balance with a precision of up to 0.1 g and numbered (use can also be made of a graduated cylinder to measure the volume of the fractions, and the calculation made in millilitres).

First distillation. The entire mixture and boiling stones are put into the flask. Then it is carefully heated. The heating of the flask during distillation is so controlled that the distillate enters the receiver at 30-40 drops per minute.

By successively changing the receivers, three fractions having definite temperature ranges are collected. These ranges are determined in the following way: the difference in the boiling points of the pure substances which constitute a given mixture is found, and then it is divided by three, i.e., by the number of fractions which are to be separated. For instance, the boiling point of pure benzene is 80.2°C , while that of pure toluene is 110.6°C . The difference in the boiling points of these substances is 30°C . Dividing this difference by three, 10°C ranges are obtained, and each fraction is separated in them.

Consequently, when a mixture of benzene and toluene is to be distilled, it is necessary to take fractions in the following temperature ranges: *I.* $80\text{--}90^{\circ}\text{C}$; *II.* $90\text{--}100^{\circ}\text{C}$; *III.* $100\text{--}110.6^{\circ}\text{C}$. Fraction *I* contains mainly benzene, fraction *II*, a mixture of benzene and toluene, and fraction *III*, mainly to-

luene. When the fractions are being separated, the receivers are changed as soon as the thermometer shows the upper limit of a fraction's temperature range. Distillation is stopped when 1-2 ml of the distilland remains in the flask because a substance cannot be distilled to dryness. After distillation is completed, the fractions obtained and the residue in the distilling flask are weighed or their volume is measured. The total mass (or volume) of the distillation products is calculated, and then the ratio of the mass (or volume) of each fraction to the total mass (or volume) of the distillation products is estimated (in percentage). All these data are written down in the laboratory notebook.

Second distillation. Fraction *I* is put into a clean and dry distilling flask and distilled in the above-mentioned temperature range, i.e., 80-90 °C. The distillate to 90 °C is collected in the first receiver, the burner is turned off, the flask is allowed to cool slightly, and fraction *II* is added through the dephlegmator to the residue in the distilling flask. The flask is then heated again, the distillate driven off to 90 °C is collected in the first receiver, and the distillate driven off within the 90-100 °C range in the second receiver. The burner is then turned off and, as the flask cools, fraction *III* is added to the residue in the distilling flask. Distillation is resumed, collecting the distillate to 90 °C in the first receiver, the distillate to 100 °C in the second receiver, and the distillate to 110.6 °C in the third receiver. After finishing the second distillation, the fractions obtained and the distillation residue are weighed (or their volume is measured), the total mass (volume) of the products of the second distillation is calculated, and the percentage of the fractions obtained with respect to the total mass (volume) of the product of the second distillation is estimated. These data are also written down in the laboratory notebook.

Subsequent distillations can be carried out similarly, but much of the substance is lost when distillation is carried out many times.

After completing the last distillation, it is necessary to indicate the yield of fraction *I* (benzene) in percentage of the amount of benzene which was in the mixture, and the yield of fraction *II* (toluene) in percentage of the amount of toluene in the mixture.

RECTIFICATION

Neither simple nor fractional distillation make it possible to completely separate the components of a mixture and obtain them in pure form. Both components are volatile, and therefore both of them pass into vapours, although to a different extent. Rectification is used for separating the components most thoroughly.

Rectification is repeated distillation which is carried out in the counterflow of a vapour and a liquid. When the rising vapours come into contact with the dripping liquid, the vapours are partially condensed and the liquid is partially evaporated. In this case, mainly the high-boiling component condenses from the vapours, and mainly the low-boiling component evaporates from the liquid. Thus, the dripping liquid is enriched by a high-boiling component, while the rising vapours, by a low-boiling component. As a result, the vapours coming out of the apparatus are an almost pure low-boiling component. These vapours condense. A part of the condensate returns into the flask as reflux, while the other part is discharged as a distillate.

For rectification, use laboratory rectifying columns of different designs (e.g., Fig. 3.14) that are connected to the distilling flask,

Rectifying columns are used to separate liquids whose boiling points differ only by 2°C .

The efficiency of a column depends on its height, the nature of packing, the amount of reflux and the efficiency of heat insulation. Simplified rectifying columns packed with pieces of glass tubing, glass beads, and so forth, are often used in the laboratory.

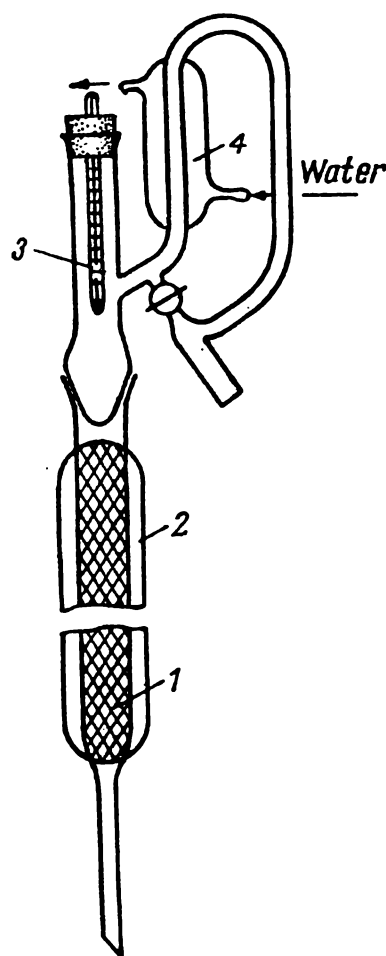


Fig. 3.14. Rectifying column:

1—packing; 2—insulation;
3—thermometer 4—condenser

But not all substances which boil at different temperatures can be separated by distillation. This applies to substances which form the constant-boiling or *azeotropic* mixtures, e.g., ethyl alcohol-benzene (32 : 68); ethyl alcohol-chloroform (7 : 93); ethyl alcohol-carbon tetrachloride (16 : 84); ethyl alcohol-water (95 : 5), and chloroform-water (97 : 3). There are binary and ternary mixtures with a definite proportion of the components whose composition of saturated vapour and of the liquid is the same.

Such mixtures boil at a temperature which is lower or higher than the boiling point of each component. Azeotropic mixtures are very common, and the boiling point of most of them is lower than that of each component. For instance, a mixture which consists of 7 parts of ethyl alcohol and 93 parts of chloroform boils at 60°C , although alcohol boils at 78°C , while chloroform, at 80°C .

Azeotropy is due to a complicated interaction between molecules in a liquid that is based on cohesive forces, association and solvation. It is used for various purposes, e.g., for separating and purifying various substances, removing water from the reaction mixture and dehydrating solvents.

To separate a component from the azeotropic mixture, use can be made of the freezing-out technique as well as of a chemical reaction in which only one component of the mixture participates.

3.5. CHROMATOGRAPHY

At the turn of this century, the Russian scientist M. S. Tswett discovered a technique of analyzing substances by adsorption chromatography and laid the foundations of *chromatography*, an effecting method of separating and purifying substances.

This method is based on the fact that an adsorbent adsorbs substances with different force when a test solution or gaseous products are passed through. There are three types of chromatography, adsorption, partition and ion exchange, in conformity with the interaction between the adsorbent and the substance in the solution. Usually, mixed processes occur with the predominance of one of them. For instance, ion exchange processes are important in adsorption chromatography, and adsorption and ion exchange processes in partition chromatography.

Chromatography is now widely used, especially for separating small amounts of substances which are similar in their composition and properties, for purifying compounds which have a high boiling point or are thermally unstable, and for separating some natural substances, such as natural dyes and amino acids.

ADSORPTION CHROMATOGRAPHY (COLUMN CHROMATOGRAPHY)

The principle of adsorption chromatography is that when a test solution or gaseous products are passed through a high and relatively narrow column packed with a finely ground or powdery adsorbent, the substances are adsorbed in conformity with their tendency to be adsorbed in definite sequence.

The so-called *chromatogram* is formed, and it is *developed* by passing a certain amount of a pure solvent, usually the one in which the test substance is dissolved, through the column.

The solvents most frequently used for developing adsorption chromatograms can be arranged in the following order: petroleum ether, gasoline, carbon disulphide, carbon tetrachloride, benzene, chloroform, ether, ethyl acetate, acetone, propyl alcohol, ethyl alcohol, methyl alcohol, water and pyridine. When the column is washed with a solvent, the solutes are distributed through the column; in this case, there are bands or zones which move downward along the path of movement of the developing liquid at a rate which depends on the ability of a given substance to be adsorbed by the adsorbent in the column. This property usually differs for various substances, and therefore the bands are more or less clearly separated from one another.

When coloured substances or substances which become coloured in adsorption are being separated, coloured bands originate directly on colourless or poorly coloured adsorbents. If it is visually difficult to determine the position of the bands on the adsorbent column, ultraviolet rays are used because many substances glow in ultraviolet light. It is therefore expedient to have columns made of quartz glass, which passes these rays through.

Fluorescing adsorbents are used if colourless and non-fluorescing substances are involved. For this purpose, a substance which

glows in ultraviolet light, such as zinc sulphide or a fluorescing organic dye, is added to an ordinary adsorbent.

Various techniques are used for separating substances from a developed chromatogram. When work is being done with coloured substances, or when the boundaries of individual bands can be easily distinguished by fluorescence in the ultraviolet light, the adsorbent with the adsorbates is carefully pushed out of the column and, after cutting it into bands, substances are extracted from each band.

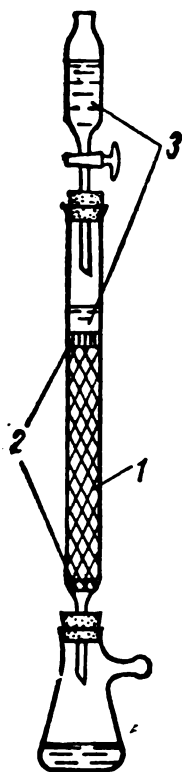
Another technique of developing the chromatogram is by eluting the adsorbates, i.e., they are washed out of the column by solvents and are collected as individual fractions of solutions (eluates). The separated substances in these fractions are then detected or quantitatively determined by the appropriate chemical or physical methods. When such a "liquid chromatogram" is being taken, the strongly adsorbed substances appear in the eluate later than the less strongly adsorbed substances.

In the so-called displacement development, a solvent is used for eluting substances to be separated from the column in the sequence of their weakening bonds with the adsorbent. Besides these methods of separating substances from chromatograms, there are diverse techniques in which each of these methods is employed.

In the laboratory, a simple apparatus shown in Fig. 3.15 is usually used for

Fig. 3.15. Apparatus for adsorption chromatography:

1—adsorbent; 2—cotton wool pad; 3—solvent



chromatography. A glass tube with a narrow lower part is used as a chromatographic column. To maintain the necessary temperature in elution, use is occasionally made of a column designed like an ordinary Liebig condenser, i.e., it is washed with water of a definite temperature. The dimensions of a tube are fixed in conformity with the conditions of an experiment and the requirements. In any case, the tube should not be too wide; otherwise, band separation is less distinct when the chromatogram is developed. A loose pad of ordinary cotton or glass wool for holding the adsorbent is put into the lower part of the tube, while a dropping funnel is attached to the upper part of the tube by a rubber stopper.

The adsorbents most commonly employed are aluminium oxide, which is used for separating neutral and basic substances, and

activated charcoal, which is used for adsorbing substances from aqueous or alcoholic solutions. Less use is made of silica gel, magnesium oxide, calcium hydroxide, carbonates and sulphates of alkaline-earth and alkali metals, glucose, lactose, etc.

To successfully separate a mixture, it is very important to fill a chromatographic column with a sufficiently homogeneous adsorbent; in this case, the smaller the particles, the clearer the boundary of bands when the chromatograms are being developed. The resistance of the column, however, simultaneously increases. To avoid this disadvantage, it is occasionally expedient to add certain grades of infusorial earth with insignificant adsorptivity to the ground adsorbent. Air bubbles and cracks in the adsorbent and the irregular packing of the latter negatively affect chromatographic results.

A column can be packed by two methods: dry and wet.

Dry Packing Method. A column is washed with a hot chromic acid mixture and then with distilled water, and dried. A dry, thoroughly sifted ground adsorbent is put into a column in small equal portions and is packed with a closely fitting pestle. The column is so packed that one-third of the tube is empty.

After filling the column, the adsorbent is wetted with a solvent and again pressed with the pestle. Then its surface is levelled out and a piece of cotton is put on top of it to prevent the upper layer of the adsorbent column from being washed out by the solvent. A solvent layer of 5-7 cm is poured over the cotton; otherwise, cracks are formed in the adsorbent.

Wet Packing Method. In this method, an adsorbent suspension in the appropriately selected solvent is put into the column. The adsorbent and the solvent are stirred well with a mechanical stirrer and the suspension formed is put into the column through a separatory funnel while continuously stirring. A loose piece of cotton is then put 1 cm above the adsorbent surface, and a solvent layer of 5-7 cm is poured over it.

A solution consisting of a mixture of substances in a suitable solvent is carefully poured through a dropping funnel into the prepared column. The ratio of the given mixture to the adsorbent should be about 1 : 100. As soon as the solution is absorbed, a pure solvent is poured into the funnel and the development of the chromatogram is commenced. In modern laboratories, the eluate is collected in the form of a large number of small portions of 0.5-10 ml. This process is carried out automatically by means of special collectors. The solvent is then removed from the eluate by distillation or evaporation, separating the pure substance. If the component thus separated is a liquid, it is distilled and its boiling point, refractive index and density are determined. If a solid is

separated, its melting point is determined and, whenever necessary, recrystallization is carried out.

Separation of *o*-, *m*- and *p*-Nitroanilines. The chromatographic column (see Fig. 3.15) is filled by the dry packing method with 50 g of calcium hydroxide. A solution of a mixture of *o*-, *m*- and *p*-nitroanilines (0.15 g each) in 50-60 ml of petroleum ether is passed through an adsorbent at a rate of 1-2 drops per second. The chromatogram is developed by 200 ml of petroleum ether; in this case, three bands are developed: the upper light yellow band (*p*-nitroaniline), the middle yellow band (*m*-nitroaniline), and the lower yellow-brown band (*o*-nitroaniline).

To separate nitroanilines, the bands are eluted by a mixture of 4 ml of methyl alcohol and 200 ml of benzene, adding it dropwise through the dropping funnel. As the bands are washed out, the eluate fraction is collected in different receivers. Afterwards, the solvent is distilled from every fraction, the yield and the melting point of each separated substance are determined and, if need be, are recrystallized.

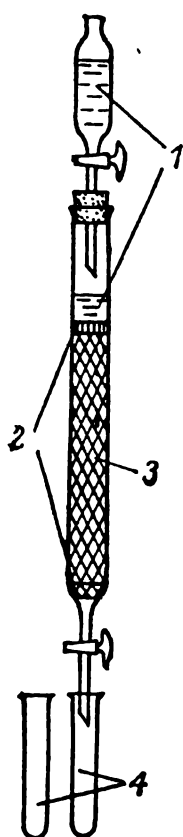


Fig. 3.16. Apparatus for partition chromatography:

1—solvent; 2—cotton wool pad; 3—silica gel; 4—test tubes for collecting the eluate

PARTITION CHROMATOGRAPHY

Partition chromatography consists in the fractional separation of a mixture whose components have different distribution coefficients between two immiscible solvents.

The carrier used is usually silica gel; starch and cellulose are used less frequently because of their inconsiderable adsorptivity with respect to many substances.

A solid carrier is so impregnated with a solvent that it appears to be still dry. This solvent is said to be stationary. The test mixture is dissolved (or suspended) in another solvent, which is said to be mobile or moving, and a solution (or a liquid gruel) is uniformly passed through the column (Fig. 3.16). When the solution is adsorbed, the column is washed

with a pure mobile solvent until the components of the mixture of substances form bands in the column or until the substances are in the solvent which drips from the lower end of the column (this is detected by specific reactions). The components are then successively eluted and the eluate fractions are collected in different receivers as the bands are washed out. The solvent is removed from the fractions by distillation or evaporation, separating pure substances.

Unlike adsorption chromatography, partition chromatography is especially advantageous for separating the adjacent members of the homologous series that differ from one another mainly in solubility.

PAPER CHROMATOGRAPHY

A particular case of partition chromatography is paper chromatography, which is used mainly for qualitatively analyzing mixtures of organic substances. This type of chromatography is carried out very simply and, what is more, with very small amounts of substances.

Pure cellulose in the form of special filter paper is used as a carrier for the stationary solvent. It should be highly pure and uniformly dense. The stationary solvent in paper chromatography is in most cases water, which is always present in filter paper. However, another solvent can be a stationary phase on paper. The moving solvents most commonly used are butyl and amyl alcohols, phenols, cresols and isobutyric acid or their mixtures, which are preliminarily saturated with water.

Paper chromatography is carried out in the following way: a drop of a solution of a test mixture is deposited on paper and dried. The paper is then put in a closed vessel in which it is continuously wetted with a solvent. The solvent uniformly moves along the paper in one direction, and the substances which are in the composition of the test mixture move along the paper at a different rate in the same direction, forming separate bands or spots. To obtain good results in paper chromatography, the following conditions must be met:

1. Very pure solvents must be used.
2. The spots must be 0.5-1 cm when doses are large, and 0.2 cm when they are small.
3. The chromatographic chamber must be gas-proof, and must be saturated with the vapours of both phases.
4. Constant temperature must be maintained during an experiment so as to prevent the liquid phases from separating.
5. There must be cleanliness so as not to contaminate moist chromatograms by impurities when they are being transferred.

Every component of a mixture is identified by the coloured spot by calculating the value of the distribution coefficient R_f . This coefficient is characterized by the ratio of the distance x (mm), which is travelled by a substance from the line where it was deposited (starting line) to the centre of the spot, to the distance y (mm), which is travelled by a solvent from the same starting line

to the front of the solvent. The value of R_f is calculated by the formula:

$$R_f = \frac{x}{y}$$

The distribution coefficient of every compound is a characteristic value. For a large number of substances, the values of R_f are given in special tables, and therefore the substance to which a found value corresponds can be easily determined. The values of R_f substantially depend on the temperature, the solvent, the quality of the paper and other factors. Therefore, in identifying substances, a sample of the pure preparation of the same substance, known as the reference spot, should be simultaneously chromatographed for comparison. In this technique, drops of the reference

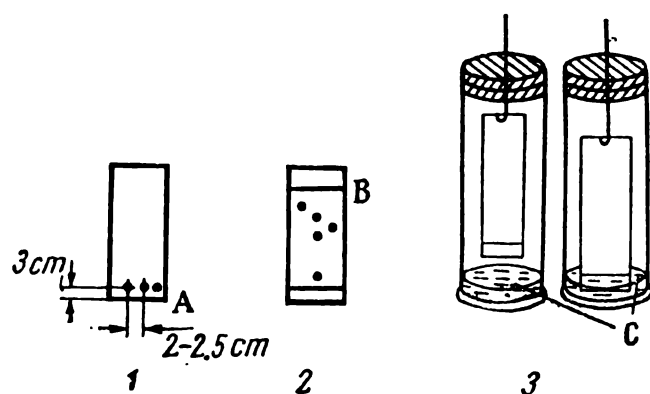


Fig. 3.17. Performance of ascending paper chromatography:

1—paper before chromatography; 2—paper after chromatography; 3—apparatus for ascending chromatography; A—starting line; B—solvent front boundary; C—solvent

spot are deposited on the same starting line on both sides of the drop of the mixture 3-4 cm away from it. After chromatography and the development of the spots, the position of the spots of the components of the test mixture is compared with that of the spots of the reference solution.

There are various methods, characterized by particular techniques, of carrying out paper chromatography: ascending chromatography, descending chromatography and circular chromatography.

The simplest case of paper chromatography is ascending chromatography, with water acting as a stationary solvent. It is carried out in the following way: a strip of filter paper is so cut that it fits the size of the cylinder used for chromatography (the strip is usually 15-30 mm wide and 300-500 mm long). The starting line is drawn with a pencil 3 cm away from the lower end of the paper strip. The starting points, 3 mm in diameter, are plotted in small circles on this line 2-2.5 cm away from one another and from the edges of the strip. The test solution of a substance in water or a highly volatile solvent should have an approximately 1 per cent concentration of each component of the mixture. A special pipette or a capillary tube is used for depositing drops of the test substance on every starting point.

A layer of a mobile solvent is then poured on the cylinder bottom (the height should be about 2 cm) and the dried strip is so

suspended that it touches neither the cylinder sides nor the liquid (Fig. 3.17), and the strip is left in this position overnight to allow the atmosphere in the cylinder to be saturated with the vapours of a given solvent.

On the next day, the lower end of the strip is immersed by 0.5 cm in the mobile solvent, which rises by about 20-25 cm under the action of capillary forces in 12-18 h. The strip is then taken out, the upper boundary of the front of the solvent is marked with a pencil, and the chromatogram is dried. If the spots are not coloured and do not fluoresce in ultraviolet light, they are developed by being sprayed with indicator reagents from an atomizer that produce a colour with the appropriate components.

ION EXCHANGE CHROMATOGRAPHY

Ion exchange chromatography is based on exchange between the ions in a solution and the ions of some absorbers known as ion exchangers. Examples of such substances are sulphuretted carbon, polymethacrylic acid and the products of condensation of various substituted phenols and aminophenols with formaldehyde. Many ion exchangers are used in both water and organic solvents. Before being used, they are ground and purified; to this end, an ion exchanger is successively treated with acid and alkali. The pure and dry ion exchanger obtained is suspended in water and the chromatographic column is filled with this suspension as indicated earlier (p. 82). A solution of the test mixture is passed through this column at a rate of 1 ml/min. The chromatogram is then developed by elution.

Ion exchange chromatography is of great importance in studying related compounds and is used mainly in analytical chemistry.

Chapter 4

DETERMINATION OF THE PRINCIPAL CONSTANTS OF ORGANIC COMPOUNDS

To identify organic substances and prove the purity of a substance, use the methods for determining the physical constants of organic compounds. In most cases, in order to determine the degree of purity of a crystalline substance, it is enough to determine its melting point, and of a liquid, its density, boiling point and refractive index.

4.1. MELTING POINT

The melting point is the temperature at which the liquid phase is first noticed. The temperature at which the liquid phase appears and the temperature at which a substance completely melts should not differ by more than 0.5°C for pure compounds. When a substance has even inconsiderable impurities, its melting point occasionally sharply drops and the substance melts in a wider temperature range. This phenomenon is used to identify two substances with the same melting point.

For that purpose, different amounts of two substances are thoroughly mixed. If the melting point of the "mixed sample" remains the same, it is concluded that both substances are identical. If the melting point of the sample drops, it means that the substances are not identical. The identification of a test substance by the melting point of a mixed sample is so generally accepted that the technique is often believed to be reliable for drawing a conclusion.

Many organic substances decompose as they melt. This is usually detected by the coloration of the melt or the liberation of gases. Decomposition is a chemical process. The temperature at which it occurs is especially dependent on the duration and rapidity of heating, as well as on how closely a substance is packed in a capillary tube, the diameter of the capillary tube, etc. In reference literature, the value of the melting point is often given together with the letters "dec" to characterize substances which melt with decomposition.

The melting point of a substance and its structure are interdependent. For instance, symmetrically arranged molecules melt at a higher temperature than their isomers.

The melting point of an organic crystalline substance can be determined in a capillary tube. About 0.001 g of a test substance

is put into a small capillary tube which is sealed at one end. The capillary tube is drawn out of thin-walled glass tubing with a diameter of 10-12 mm, which has been thoroughly cleaned and dried. The test substance is finely ground in a mortar or on a watch glass. A small amount of the substance is then collected in the capillary tube by its open end, and then the tube is dropped with its closed end down into a glass tube which is 80-90 cm long and is placed vertically on the laboratory bench. This filling operation is repeated several times until the capillary tube has a well

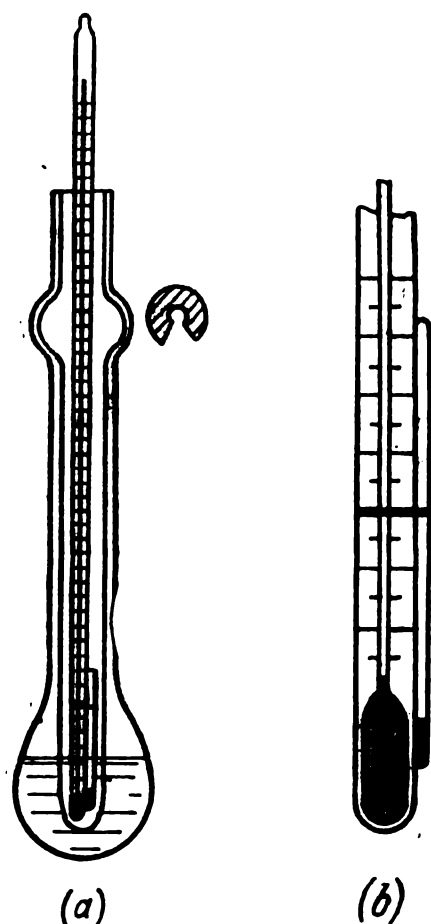


Fig. 4.1. Apparatus for determining the melting point:

a—thermometer with a capillary tube placed in a test tube; *b*—attachment of a capillary tube with a substance to a thermometer

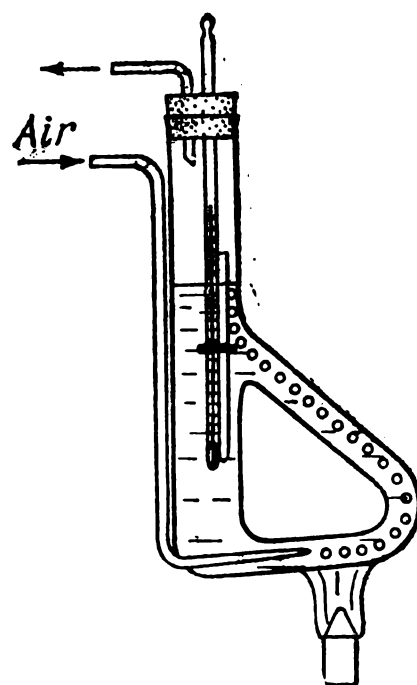


Fig. 4.2. Thiele melting point apparatus

packed column of the substance about 2 mm high. The capillary tube thus packed is so secured on the thermometer that the sample of the substance is on the same level with the thermometer bulb. A rubber band is usually used for attaching the capillary tube to the thermometer.

The melting point of the substances being sublimed is determined in capillary tubes both ends of which are sealed.

The simplest apparatus for determining the melting point is represented in Fig. 4.1. It consists of a round-bottom flask with side openings for the evaporation of the liquid being heated. The

capillary tube is put together with the thermometer into a test tube which is in the flask. The flask neck should be long so as to prevent the liquid from splashing out and reduce the error in the thermometer reading of the protruding mercury column.

It is far better to determine the melting point in Thiele's apparatus (Fig. 4.2), in which heat is transferred more uniformly, than by the foregoing method.

The heat transfer medium of a liquid is either water, if it is known that the melting point of the test substance is below 100°C,

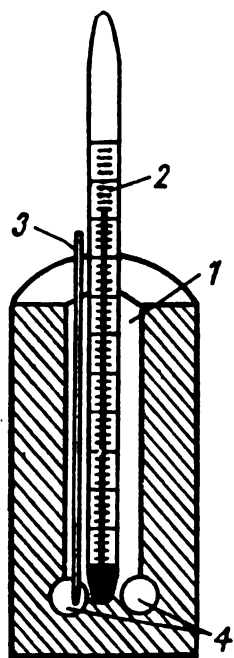


Fig. 4.3. Metallic unit for determining the melting point:

1—channel for a thermometer; 2—thermometer; 3—capillary tube; 4—inspection holes

or concentrated sulphuric acid, which makes it possible to determine the melting point to 250°C. Sulphuric acid darkens when it is used for a long time, and a small saltpeter crystal is put into it for decolorization. Care should be taken when determining the melting point in apparatus containing sulphuric acid, because hot sulphuric acid is dangerous if an apparatus gets broken. Therefore, *safety glasses should be worn* when working with *sulphuric acid*. Besides water and sulphuric acid, use is made of paraffin oil (dec. 220°C). But paraffin oil is a poorer heat conductor than sulphuric acid, and therefore an apparatus may be heated irregularly. It is best to use silicone oil. Oil must not be used when working with a substance which melts above 300°C because it darkens rather rapidly and, in this case, it is better to use a mixture of potassium nitrate (54.5 per cent) and sodium nitrate (45.5 per cent). Such a mixture melts at 218°C and can be heated to 600°C.

When the apparatus is assembled, it is slowly heated on an asbestos net by a small burner flame and attention is paid to the elevation of temperature and the state of the column of a substance in the capillary tube. While observing the substance in the capillary tube, a record is kept of all its changes, such as colour change, decomposition, sticking together, caking and wetting. The burner is removed when the test substance becomes wet and begins to noticeably contract. Melting begins when the first drop appears in the capillary tube, and ends when the last small crystals of the substance disappear. It is expedient to use a metallic unit (Fig. 4.3) made of brass or copper for determining the melting point of substances which melt above 300°C. The lower part of the unit is heated by a burner. A thermometer is put into the

cylindrical channel, and two capillary tubes containing a substance, into grooves. An eye is kept on the melting process in the capillary tubes through inspection holes which are covered with small pieces of glass.

4.2. BOILING POINT

The boiling point is the temperature at which the vapour pressure of a liquid is equal to atmospheric pressure. It considerably depends on the molecular weight of a substance, its structure and composition, intermolecular interaction and pressure.

The simplest apparatus for determining the boiling point is a simple distillation apparatus consisting of a round-bottom flask, a thermometer, a condenser, a bent adapter and a receiver. A liquid whose boiling point is to be determined is poured into a round-bottom flask up to a quarter of its volume. The thermometer bulb is slightly above the liquid surface. If the boiling point of the solution is to be determined, the thermometer bulb is immersed in the liquid. To prevent the liquid from being greatly superheated, the appropriate baths are used for heating when the boiling point is to be determined. The difference in temperature between the beginning and the end of boiling should not be greater than 0.5 °C for pure substances. When the liquid boils in a wide temperature range, it means that the liquid is a mixture.

When the boiling point is to be determined, account should be taken of the correction for the deviation from atmospheric pressure. Reference literature has tables of corrections for the boiling points of many substances under different pressures, giving their boiling points at 760 mm Hg. If such tables are unavailable, the correction for the deviation from atmospheric pressure can be calculated from the fact that the boiling point of many substances at 760 mm Hg changes by about 3/80 with a change in pressure by 1 mm Hg.

If pressure A , at which the boiling point is being determined, is less than 760 mm Hg, correction n_1 for deviation can be calculated accurately enough by the equation:

$$n_1 = \frac{3}{80} (760 - A)$$

If pressure A is higher, correction n_2 is obtained from the equation:

$$n_2 = \frac{3}{80} (A - 760)$$

Sivolobov's method is used when small amounts of a substance are involved. In this method, 0.5 ml of the test liquid is poured into a glass tube about 6 mm in diameter, and then to determine

the melting point, a capillary tube is immersed in the liquid with the open end down. The tube is attached to the thermometer as shown in Fig. 4.4. The thermometer is put into the apparatus used for determining the melting point. On slow heating, bubbles of vapour come out of the capillary tube faintly at first, and then rapidly. The boiling point is the temperature reading at the moment when bubbles are rapidly formed. The accuracy of this method is $\pm 5^\circ\text{C}$.

The boiling point can be accurately determined by ebullioscopes (Fig. 4.5). When they are used, the liquid is heated with a reflux

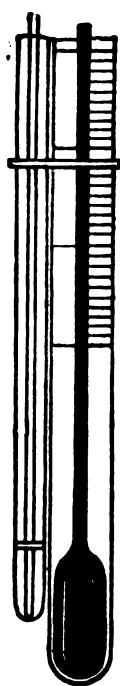


Fig. 4.4. Attachment of a tube with a substance to a thermometer when determining the boiling point by Sivolobov's method

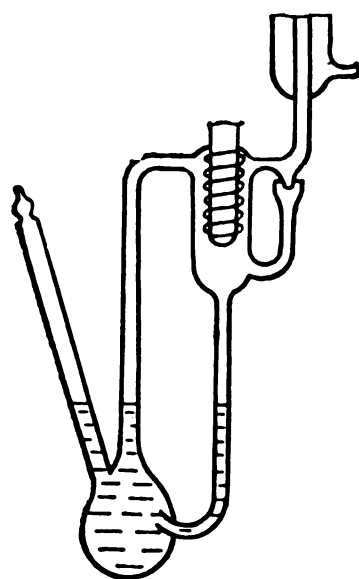


Fig. 4.5. Ebullioscope

condenser until it boils and its temperature is measured; when the ebullioscope is properly designed, heat is not lost and vapours are not superheated. These devices do, however, usually require large amounts of a substance (several millilitres).

4.3. SPECIFIC GRAVITY

Specific gravity is one of the most important physico-chemical characteristics of a substance, and its determination is one of the most common operations in the laboratory. Density is of great importance in identifying many liquid isomers, characterizing mixtures, calculating molecular refraction, etc.

The density of a substance is the ratio of its mass to its volume:

$$\rho = \frac{m}{V}$$

where m = mass of a substance;
 V = volume of a substance.

In the laboratory, use is usually made of specific gravity, which is the ratio of the density of a given substance to that of another substance under definite conditions. The specific gravity d of a substance is usually determined with respect to the density of distilled water:

$$d = \frac{\rho}{\rho_w}$$

where ρ = density of a substance;
 ρ_w = density of distilled water at 4 °C.

Specific gravity is expressed by an abstract number. Since all bodies change their volume in conformity with temperature, it is quite clear that the density value will vary as a result of a change in the temperature at which it is being determined. Therefore, the temperature at which a determination is made and the temperature of water whose volume is taken as unity are always given. Specific gravity is usually determined at 20 °C or 15 °C and denoted by the appropriate subscript and superscript, e.g., d_4^{15} , which indicates that specific gravity has been determined at 15 °C and the density of water at 4 °C has been taken as unity for comparison.

Specific gravity can be determined by areometers, pycnometers, a hydrostatic balance, etc. In the simplest cases, areometers (Fig. 4.6) are used for quickly determining the specific gravity of a liquid. Density is determined by areometers on the basis of the fact that if a body immersed in a liquid does not sink, but floats, the depth of its immersion depends on the density of a given liquid. The areometer is a glass tube which expands at the lower end and whose end has a glass bulb filled with shot or some special mass so that the areometer will be in a vertical position during measurement. The upper narrow part of the areometer has a division scale. The less the specific gravity of a liquid, the further the areometer is immersed in it, and therefore the top of the scale shows the least value of specific gravity, and its bottom, the greatest value. Areometers sometimes have thermometers (Fig. 4.6b), and this makes it possible to simultaneously measure the temperature at which a determination is being made. To determine specific gravity by an areometer, the liquid is poured into a glass cylinder whose volume is at least 0.5 l, and the areometer is carefully immersed in it. The areometer must be in the centre of the cylinder and should by no means touch the sides or the bottom of the cylinder (Fig. 4.7). The division against which the upper meniscus of the liquid stops is the value of specific gravity.

Pycnometers (Fig. 4.8) are used for determining the specific gravity of liquids with a precision of up to the fourth decimal

place. First, the mass of an empty pycnometer is determined on the analytical balance with a precision of up to 0.0001 g. Then the mass is determined when the pycnometer is filled with water and afterwards with the test liquid, thus finding the masses of equal volumes of the test liquid. The value of specific gravity d is obtained by taking the ratio of these masses:

$$d = \frac{p_1 - p}{p_2 - p}$$

where p = mass of the empty pycnometer;

p_1 = mass of the pycnometer with the test liquid;

p_2 = mass of the pycnometer with water.

Measurements should be taken twice at the same temperature.

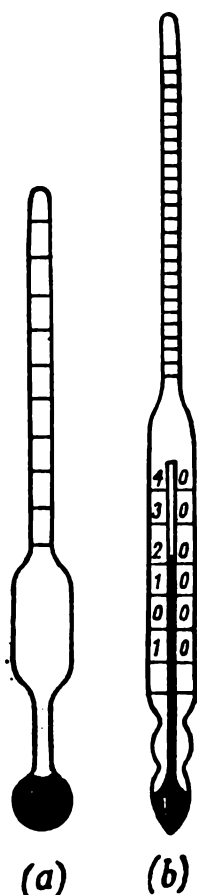


Fig. 4.6. Areometers:
a—without a thermometer; b—with
a thermometer

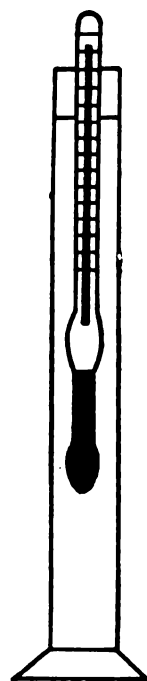


Fig. 4.7. Position of the areo-
meter when measuring specific
gravity

The hydrostatic balance can be used for determining the specific gravity of a liquid and a solid. The ordinary analytical balance can serve as such a balance. To determine the specific gravity of a liquid, a cylindrical vessel with the test liquid in it is put on the left-hand balance pan, while a cylindrical glass plumb is suspended on the stirrup which holds the bow with the pan.

The plumb is at first weighed in air, and then its weight is determined in distilled water and in the test liquid, and the specific

gravity of a given liquid is found by the formula:

$$d_t^t = \frac{p_0 - p}{p_0 - p_w}$$

where p_0 = weight of the plumb in air;

p_w = weight of the plumb in distilled water;

p = weight of the plumb in the test liquid.

To determine the specific gravity of a solid, the latter is suspended instead of the plumb and weighed in air and distilled

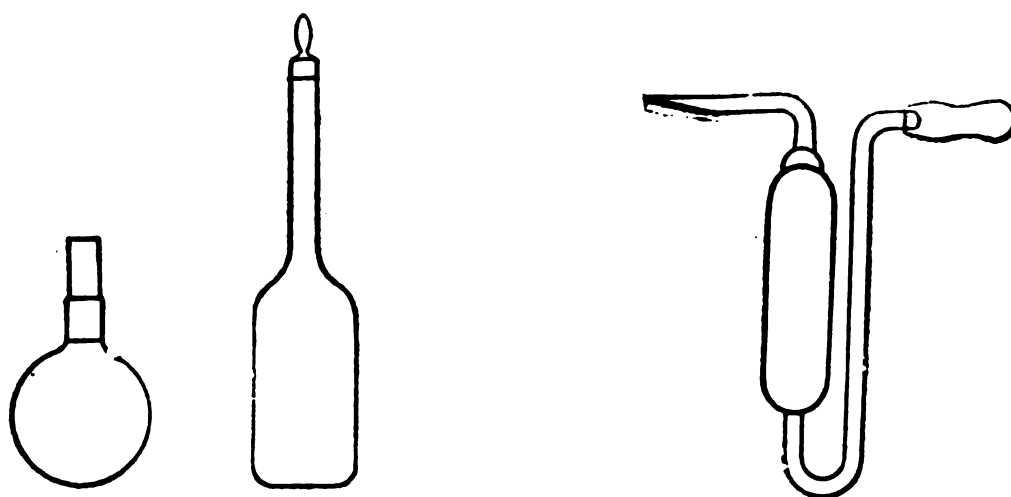


Fig. 4.8. Pycnometers

water. If a body in air is counterbalanced by weight p , and in water, by weight p_w , its specific gravity will be:

$$d_t^t = \frac{p}{p - p_w}$$

i.e., the weight of the body divided by the weight of the water it displaces.

4.4. REFRACTIVE INDEX

The refractive index is widely used for identifying and checking the purity of liquid substances, analyzing binary liquid solutions whose dependence of the refractive index on the composition of the solution is known, determining the concentrations of sugar in aqueous solutions, and in many other cases.

The refractive index n is a constant value for a given substance that is equal to the ratio of the sine of the angle of light incidence on the interface to the sine of the light refraction angle (Fig. 4.9):

$$n = \frac{\sin \alpha}{\sin \beta}$$

The initial medium is usually air, i.e., the incidence of light on the refracting medium is through air.

The refractive index greatly depends on temperature and sharply changes in conformity with the light wavelength. For instance, it is 4×10^{-4} for organic liquids when temperature rises by 1°C . Therefore, the refractive index is measured in monochromatic light at constant temperature; in this case, the subscript is the accepted letter notation of the spectral line, in whose light the measurement has been taken, or of the wavelength. The superscript is the temperature, e.g., n_D^{20} (the refractive index n is usually given for the spectral D line of the yellow sodium flame).

Abbe's refractometer is a simple and widely used apparatus for measuring the refractive index. The refracting prism is fitted out with an illuminating prism, and the gap between them is filled with 1-2 drops of the test liquid (Fig. 4.10). Abbe's refractometer has a compensator, which makes it possible to take measurements in daylight or electric light. The precision of the measurement taken by Abbe's refractometer is 1×10^{-3} . To have such precision, it is necessary to maintain constant temperature by a thermostat during measurement.

4.5. MOLECULAR WEIGHT

The molecular weight is one of the most essential characteristics of a substance. It is the basis for determining such quantities as molar concentrations, volume, heat capacity, electrical conductivity and heat of reaction. The molecular weight is used for ascertaining the structure of a substance and making all the calculations by chemical formulas and equations.

There are many different methods for determining the molecular weight of the substances of organic compounds of any class. The most widely used ones are the cryoscopic and ebullioscopic methods and Rast's method.

To determine the molecular weight by the cryoscopic method, a weighed sample of a pure solvent is put into a vessel and its freezing point is measured. A solvent is then melted in the same vessel, a weighed sample of the substance to be determined is put into it, and the temperature of the beginning of crystallization is measured. In the ebullioscopic method, the elevation of the boiling point of the solvent, caused by the introduction of a definite amount of a test substance, is measured by the Beckmann thermometer. Then the molecular weight is calculated by formulas (a detailed account of the cryoscopic and ebullioscopic methods is given in the manuals for physical chemistry).

Let us consider Rast's method, which makes it possible to determine the molecular weight of organic compounds in an apparatus for determining the melting point. The method can be used for substances which dissolve in molten camphor and are stable

to 190°C. It consists in the determination of the lowering of the melting point of camphor when a definite amount of a test substance is dissolved in it. Only 10-60 mg of a substance are required for determining the molecular weight; the accuracy of the determination is 5-10 per cent.

Let us take the example of determining the molecular weight of naphthalene by a drop in the melting point of camphor. About 0.7-0.8 g of camphor and 60-70 mg of naphthalene are put into a small clean and dry test tube. The test tube is carefully heated on a small flame so as to fuse the substances. The test tube is then

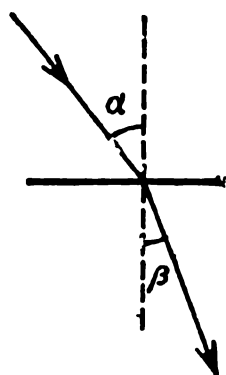


Fig. 4.9. Refraction of the light beam at the interface of two clear media

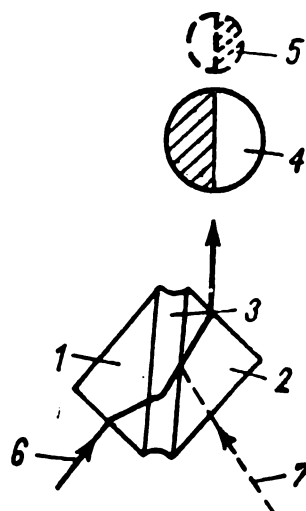


Fig. 4.10. Course of beams in the prisms of Abbe's refractometer:

1—illuminating prism; 2—refracting prism; 3—test liquid; 4—field in the observation tube when taking measurements in transmitted light; 5—ditto in reflected light; 6—course of beams when taking measurements in transmitted light; 7—ditto in reflected light

taken out of the flame and the melt obtained is stirred with a wire whose end is flattened. When the melt solidifies, a large part of it is taken out with the wire and put on a watch glass. The mass is ground and a capillary tube, about 2 mm in diameter, is packed with it (see p. 89). A sample of pure camphor is put into another such capillary tube. Both capillary tubes are attached by a small rubber band to a thermometer with divisions of 0.1°C or 0.2°C. The apparatus is then slowly heated and an eye is kept on the state of the sample by means of a magnifying glass. When the last crystals of the mixture of camphor and naphthalene melt, the temperature is recorded as the melting point of the mixture. Heating is continued so as to determine the melting point of pure camphor in the other capillary tube. The molecular weight of the test

substance (naphthalene, in this case) is calculated by the formula:

$$M = \frac{40 \times 1000m_1}{m_2(t_1 - t_2)}$$

where m_1 = weighed sample of the test substance;

m_2 = weighed sample of camphor;

t_1 = melting point of pure camphor;

t_2 = melting point of the mixture;

40 = cryoscopic constant.

In carrying out a check test, the determination should be repeated by another pair of capillary tubes.

Chapter 5

WORK WITH COMPRESSED AND LIQUEFIED GASES

5.1. GAS CYLINDERS AND HOW TO USE THEM

The laboratory gets many gases in a compressed or liquefied state in steel cylinders. Only a gas whose critical point is higher than room temperature can be in a liquefied state in a cylinder (carbon dioxide, chlorine, sulphur dioxide, ammonia, etc.). Then gas pressure remains constant as long as a liquid phase is in the cylinder. Conversely, gases which have a low critical point (oxygen, hydrogen, nitrogen, air, etc.) do not turn into a liquid under ordinary conditions and are pumped into cylinders in a compressed state under a pressure of 150-200 kg/cm²; the pressure in the cylinder gradually drops as a gas is used up. The values of the pressure under which some liquefied gases are in cylinders are given in Supplement 3.

Cylinders have two types of structure: for compressed and liquefied gases. Cylinders for liquefied gases have a siphon tube inside. Cylinders with capacities of 20 l and 40 l are most widely used. All cylinders for compressed and liquefied gases are tested from time to time at the factories which produce them; for instance, hydrogen sulphide cylinders are checked annually, chlorine and phosgene cylinders, once every two years, and other cylinders, once every three years.

Cylinders for compressed gases are made of steel and have a bottom, a neck and a shoe (Fig. 5.1). A valve for regulating gas in and out is screwed into the cylinder neck. The neck has a threaded ring on which a safety cap, protecting the valve from damage, is screwed on. The cap is sealed, while the spherical part of the cylinder has the trade mark, the type, number and weight of the cylinder, the dates of manufacture and of the next test, working and test pressures, the capacity of the cylinder and the seal of the factory's technical inspection department.

Chlorine and phosgene cylinders (Fig. 5.2) consist of the body, a screwing cap and a valve. A siphon tube extends from the neck to almost the bottom inside the cylinder, and liquid chlorine or liquid phosgene passes through it to the valve, where it evaporates. Such a structure makes it difficult to control the flow of chlorine or phosgene and retards their evaporation because the valve is cooled and covered with hoarfrost when they flow to it rapidly. To avoid this, such cylinders should be placed with the valve down in the laboratory. There are special stands (Fig. 5.3) for this purpose.

When the cylinder is in such a position, a gas passes through the siphon tube to the valve, and its flow can be exactly controlled. Otherwise, liquid instead of gas will flow out of the cylinder when the valve is opened.

Special cylinders are used for storing acetylene (Fig. 5.4). Pure acetylene can easily explode even from a jolt when the pressure is as low as 2 kg/cm². But dissolved acetylene is safe even under a pressure of 25 kg/cm². Therefore, acetylene cylinders are filled with a porous mass (activated charcoal, diatomite, chrysotile,

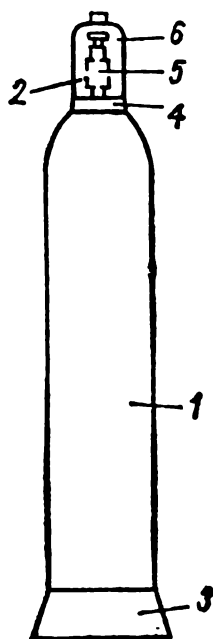


Fig. 5.1. Structure of a simple gas cylinder:

1—body; 2—ring;
3—shoe; 4—neck;
5—valve; 6—safety cap

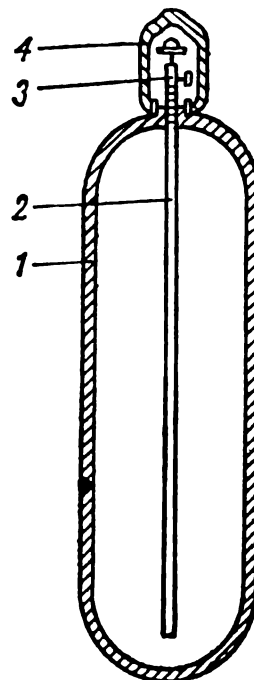


Fig. 5.2. Section of a siphon cylinder:

1—body; 2—siphon tube;
3—valve; 4—safety cap

etc.), which is impregnated with acetone, and acetylene is dissolved in this acetone under a pressure of up to 16 kg/cm². Even if there is an explosion somewhere in the cylinder, the porous mass does not allow it to spread to the entire gas and thus prevents the cylinder from bursting.

Gas cylinders have an identification colour code (see Supplement 4) to preclude errors in using them. Moreover, cylinders containing hydrogen, methane, ethane, ethylene and other flammable gases are distinguished by the fact that the side connecting tube of the valve has a left-handed thread. As a result, a dangerous error cannot be made when filling the cylinders and working with compressed gases.

To control the gas flow from the cylinder, use should be made of reducing valves (Fig. 5.5), which make it possible to have

constant pressure at the outlet. They differ in design and their through-put, the value of working pressure and their mode of operation. Laboratory reducing valves have a small through-put, i.e.,

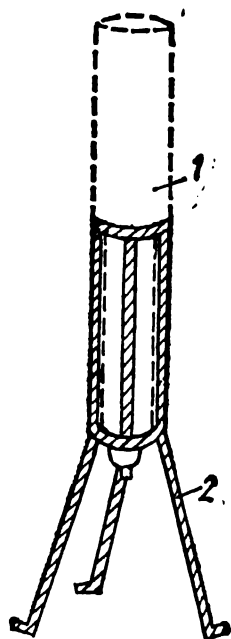


Fig. 5.3. Gas cylinder stand:
1—cylinder;
2—stand

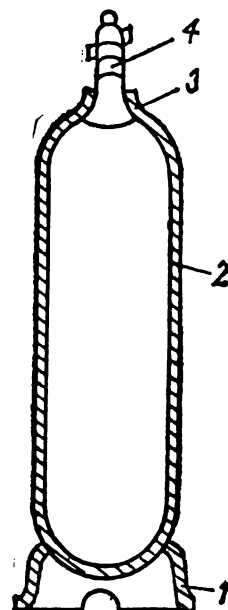


Fig. 5.4. Section of an acetylene cylinder:
1—stand; 2—body;
3—neck; 4—valve

up to $1 \text{ m}^3/\text{h}$, and are provided with a regulating screw 1 by means of which an exact gas flow rate can be set. More advanced valves have two pressure gauges, one of which shows gas pressure in the cylinder, while the other shows operating gas pressure. The reducing valves usually have the same colour as the gas cylinder.

Before starting to take a gas from a cylinder, it is especially necessary to properly fasten the cylinder and remove the seal. Then, screw off the cap with a wrench and remove it, and examine the valve and the side connecting tube of the cylinder. The valve should not have traces of fat or oil, and the thread of the side connecting tube should not be damaged. The valve is blown through, opening it by quickly turning the flywheel and immediately closing it. When flammable gas is being blown through, all the fire sources in the laboratory should be turned off and ventilation turned on.

The reducing valve is screwed on to the side connecting tube of the cylinder by means of a captive nut 3, which has a right-

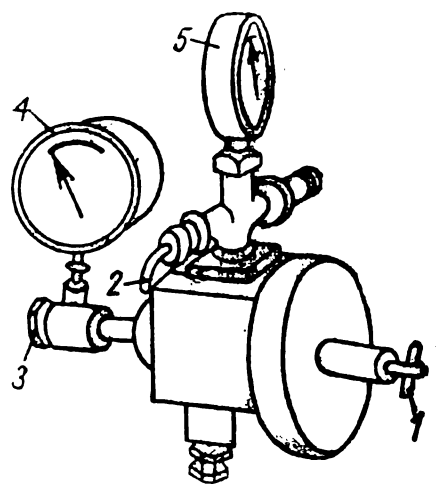


Fig. 5.5. Reducing valve:
1—regulating screw; 2—outlet connection; 3—captive nut;
4—cylinder contents gauge;
5—operating pressure gauge

handed or left-handed thread, depending on the gas for which a cylinder is intended. The regulating screw is then screwed off by turning it to the left, thus closing the reducing valve, while the cock is screwed up tight. A rubber hose is put on outlet connection 2 for gas discharge. Afterwards, the cylinder valve is opened by turning the flywheel anticlockwise. If the outgoing gas hisses, screw 1 is also screwed off. If the gas passes at nut 3, it is screwed up.

When gas no longer flows out, pressure gauge 4 shows the gas pressure in the cylinder. Screw 1 is then carefully screwed off until either pressure gauge 5 shows the necessary working pressure or the gas flows out at the required rate. Afterwards, the cock is slowly opened and gas begins to flow out of connection 2. It should be borne in mind that all the gas cannot be let out of the cylinder; gas is usually no longer taken when residual pressure in the cylinder is 1-1.5 kg/cm². After completing work, the valve is tightly closed by turning the flywheel clockwise. Then the outlet from the reducing valve is closed by weakening the regulating screw, i.e., by turning it to the left.

5.2. DOSING GASES

When working with gases in the laboratory, the gas flow rate is controlled by letting a gas pass through a bubble counter, i.e., a small vessel where a gas bubbles through a liquid. The liquid used is concentrated sulphuric acid, or, when work involves ammonia, a 50 per cent potassium hydroxide solution. If it is necessary to measure the flow rate of gas and simultaneously dry it, the bubble counter used is the Tishchenko wash bottle, which is connected to the reducing valve by means of a rubber hose.

The amount of gases is measured by their volume or mass. The gas volumes are measured either directly in graduated vessels, known as gas meters, or by the gas clock. The most frequent use is made of the liquid gas clock filled with water (Fig. 5.6) in which the gas flow rotates a cylinder connected to a counter. The clock consists of a cylindrical body, in which rotates a hollow axis with arched blades; the axis is connected to the dial needle. A gas enters the clock through the hollow axis and goes under a blade. The axis then begins to rotate. After filling the space under a blade, the gas begins to raise the next blade, etc. But, because the clock is made of metal and filled with water, the gas clock is not used for work with aggressive gases or gases which dissolve well in water.

When a gas uniformly passes through the reaction vessel, it is dosed by measuring the rate of gas flow per unit time. Rheometers and rotameters are most commonly used to this end. In rheometers

(Fig. 5.7), a pressure difference originates on both sides of a narrow opening along the path of flow of a gas when it passes through the opening (capillary tube). The pressure gradient, being proportional to the amount of flowing gas, is measured by a U-shaped manometer which is connected in parallel to the rheometer with a graduated scale for directly reading the gas flow rate.

Rotameters (Fig. 5.8) consist of a graduated tapering glass tube. The tube has a float made of ebonite or some other light and chemically stable material. The gas is passed through the rota-

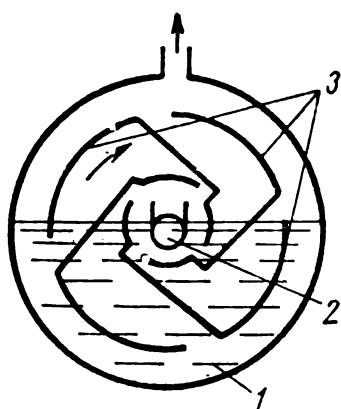


Fig. 5.6. Scheme of a water gas clock:
1—body; 2—hollow axis;
3—arched blades

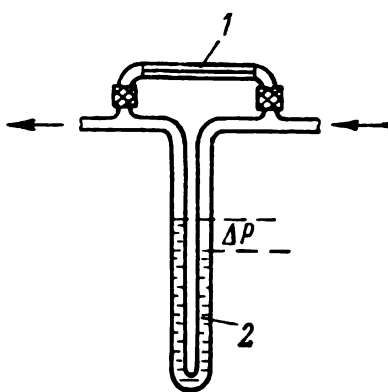


Fig. 5.7. Rheometers:
1—capillary tube; 2—liquid differential manometer

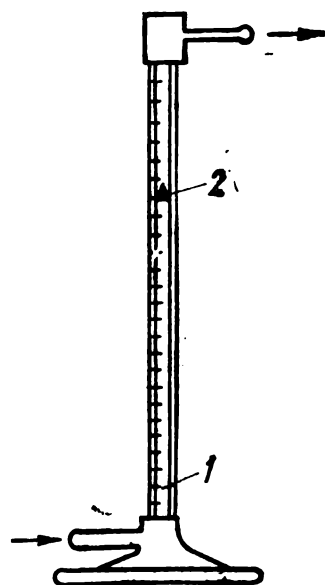


Fig. 5.8. Rotameter:
1—vertical tube; 2—float

meter upwards; in this case, the float rises along the tube under the force of gas pressure to a height which corresponds to the gas flow rate.

5.3. PURIFICATION OF GASES AND THEIR INTRODUCTION INTO AN APPARATUS

Before a gas is introduced into a reaction vessel, it must be purified by being passed through a wash bottle filled with a certain liquid.

Electrolytic hydrogen in cylinders is sufficiently pure and can be used for hydrogenation without preliminary purification. Hydrogen obtained from water gas may contain various impurities: saturated and unsaturated hydrocarbons, oxygen, nitrogen, carbon monoxide and dioxide, hydrogen arsenide, hydrogen sulphide, etc. For purification, such hydrogen is passed through a 50 per cent

potassium hydroxide solution and then through two wash bottles having a potassium permanganate solution (for oxidizing hydrogen sulphide and hydrogen arsenide), a bottle containing an alkaline solution of sodium hydrosulphite, a tube with a copper net or with platinized asbestos heated to 350-400 °C (for removing oxygen), and the Tishchenko bottle (for a dry substance) or a U-tube having calcium chloride.

Nitrogen in the cylinders usually contains about 1 per cent of oxygen, which is removed by passing the gas through an alkaline solution of pyrogallol (15 g of pyrogallol in 100 ml of a 50 per cent potassium hydroxide solution) or an alkaline solution of sodium hydrosulphite.

Carbon dioxide contains impurities of oxygen and carbon monoxide, and occasionally traces of sulphurous anhydride and hydrogen sulphide. These impurities (except oxygen) are removed by passing the gas through a tube containing cupric oxide heated to dark red incandescence, and then through a sodium bicarbonate solution and a neutral solution of potassium permanganate.

After the wash bottle, purified gases must not be immediately introduced into an apparatus because there is the danger that the reaction liquid may be sucked into the tube through which gas flows. Therefore, an empty safety flask should be placed in front of the apparatus into which a gas is being introduced. There should also be a safety vessel after the gas cylinder as well (see Fig. 2.10). Moreover, there should always be an empty bottle between the wash bottles containing alkalies and acids. The entire apparatus intended for carrying out a reaction in the gas flow should be thoroughly checked before it is used. The apparatus to be attached to the compressed gas cylinder should always have access to air because pressure in a tightly closed apparatus rapidly increases and the apparatus may explode.

5.4. SAFETY RULES IN HANDLING GAS CYLINDERS

Most of the commonly used compressed gases in combination with air, especially oxygen, easily explode. They include *hydrogen, acetylene, methane and petroleum gases*. Oxygen is also a flammable gas because it vigorously maintains combustion. Besides the foregoing gases, which can cause an explosion and a fire, there are gases which can cause poisoning (e.g., *chlorine and phosgene*). To preclude accidents when gas cylinders are used, it is necessary to take all the precautions and obey the following rules:

1. Place cylinders in special stands and as far away from heat sources as possible.

2. Protect cylinders from sudden jolts and blows, and from falling.

3. Do not lubricate reducing valves intended for oxygen with fats and organic lubricants, and do not make them airtight by means of organic spacers, because organic substances burst into flame with an explosion when they come into contact with pressurized oxygen.

4. The cylinder valve should be opened gradually; if it opens with difficulty, a hammer must not be used to open it, because this is very dangerous.

5. When beginning work, see by the colour of the cylinder and the inscription on it that it contains the gas with which work is to be done.

6. It is forbidden to repair the valve by yourself.

7. A damaged cylinder must not be used.

8. Send the cylinders regularly for inspection.

Chapter 6

QUANTITATIVE ELEMENTAL ANALYSIS OF ORGANIC SUBSTANCES

The determination of the quantity of individual elements in organic substances is known as elemental analysis, which can be carried out by the macro, semimicro and micro methods. In macro-analysis, a sample taken for combustion weighs 0.15-2 g, in semimicroanalysis, 20-30 mg, and in microanalysis, 2-5 mg. At present, wide use is made of the semimicro method, which makes it possible to work with small amounts of a substance and carry out an analysis rather quickly. The principal elements, i.e., carbon, hydrogen, nitrogen and oxygen, are determined in most cases by burning a weighed sample of a substance in a tube made of high-melting glass or quartz, and carbon and hydrogen are determined simultaneously.

6.1. SEMIMICRODETERMINATION OF CARBON AND HYDROGEN

When the semimicro method is used, a weighed sample of a test organic substance is burned in a quartz tube in a current of air and oxygen. The gaseous products of decomposition pass over the catalyst (cupric oxide or lead chromate) which is in the tube; as a result, carbon is oxidized to carbon dioxide, while hydrogen, to water. Water, which is isolated in combustion, is absorbed in a tube containing calcium chloride or magnesium perchlorate $\text{Mg}(\text{ClO}_4)_2$, which readily combines with water. Carbon dioxide is absorbed in a tube containing soda lime. The amount of water and carbon dioxide formed is determined by weighing the tube before and after the experiment. The data obtained can be used to calculate the percentage of carbon and hydrogen in the substance being considered.

ASSEMBLY

To determine carbon and hydrogen, use the apparatus shown in Fig. 6.1. All the devices of the apparatus can be divided into three groups, according to their functions. The first group consists of devices which supply oxygen and air and are fitted out with appliances for controlling pressure; the second group consists of a combustion tube and heaters, and the third group, of absorption devices

for absorbing water and carbon dioxide as well as of the Mariotte bottle, which is used to control the pressure in a system. The oxygen and air used in burning an organic substance should be collected in gas meters. A detailed description of the separate parts of the apparatus is given below.

Filling Gas Meters with Oxygen and Air. Use is usually made of glass gas meters, which consist of both a vessel for collecting a gas and a funnel with a liquid, that forces out a gas through the tube in the upper tube of the vessel. Before filling the gas meter with oxygen or air, the ground-glass joint of the funnel and all the stopcocks are lubricated with Vaseline, the lower tube is stoppered and, after taking out the funnel, water is poured into the meter until air is completely displaced. The funnel with an open

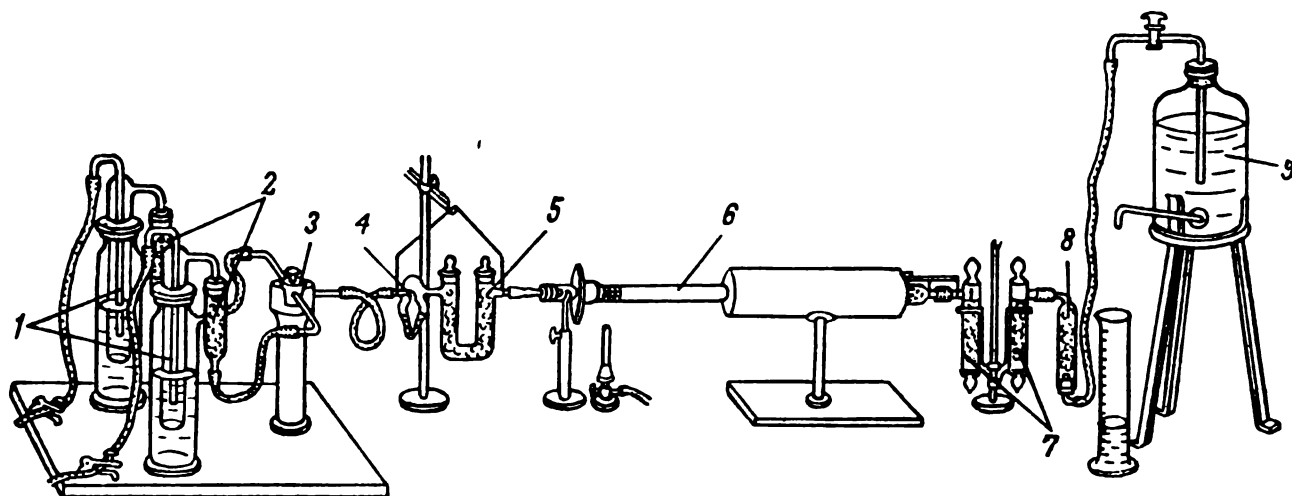


Fig. 6.1. Semimicrodetermination of carbon and hydrogen:

1—pressure regulators; 2—calcium chloride tubes; 3—three-way cock; 4—bubble counter; 5—drying U-tube; 6—combustion tube; 7—absorption devices; 8—calcium chloride tube; 9—Mariotte bottle

stopcock is then inserted and air residues are removed from it, pressurizing water by blowing air through the outlet tube. When air is removed from the tube, water is poured into the funnel and the last air bubble is removed by carefully raising the funnel.

After the gas meter is filled with water, all the stopcocks are closed, the lower tube is opened and another tube through which oxygen passes from the cylinder is put into it. The gas forces out water, which flows out of the lower tube. As soon as water ceases to flow out of the meter, the tube through which oxygen passes is immediately taken out and the lower tube is stoppered.

When the gas meter is to be filled with air, the stopcock of the upper tube is opened and water is discharged through the lower tube.

Controlling Pressure. Pressure regulators for air and oxygen are used so as to preclude the effect of the gas pressure fluctuations in gas meters and, consequently, to maintain the gas flow at

a constant rate during combustion. The pressure regulator consists of a bell-shaped vessel which has two tubes that are immersed in a cylinder one-half full of water and a small amount of potassium hydroxide.

Pressure regulators are connected to gas meters by rubber tubes. Since rubber can separate volatile organic compounds, the tubes are artificially aged; for this purpose, they are heated to 100-110 °C for an hour in a drier while simultaneously sucking air through them.

The connecting rubber tubes have screw clamps by means of which the gas flow from the gas meter is so controlled that one gas bubble comes out of the pressure regulator not less than every 10-15 sec. The outlet tubes of the pressure regulators are connected to the three-way cock, which makes it possible to feed oxygen or air to the apparatus through rubber tubes which have also been artificially aged.

To maintain a constant concentration of the potassium hydroxide solution in the bubble counter, which is connected to the three-way cock, calcium chloride tubes filled with coarse-grained calcium chloride are put between the pressure regulators and the three-way cock.

Preparation of the Bubble Counter and the Drying U-tube for Operation. The bubble counter is used for controlling the gas flow rate, and a drying U-tube with two ground-glass stoppers, filled with soda asbestos (asbestos impregnated with soda lime) and calcium chloride, is sealed to it. The tube is used for drying gases.

The U-tube with a bubble counter is first washed with a chromic acid mixture and afterwards with water and alcohol. Then it is dried and filled in the following way: the ground-glass stopper of the U-tube is taken out and a cotton wad is temporarily put through a ground-glass joint by a bent steel wire into an outlet tube sealed to the bubble counter. A piece of cotton is then put in the lowest part of the tube and calcium chloride (which is usually not too ignited) is poured on the cotton by tapping until the layer is 0.5 cm thick. The layer is then covered with a small cotton wad, and soda asbestos is poured on it up to the outlet tube. After covering the soda asbestos layer with cotton, the cotton wad in the outlet tube is replaced by a very loose cotton spacer. Larger pieces of calcium chloride are then poured on the asbestos up to the ground-glass joint, and this layer is also covered with a piece of cotton. The ground-glass joint is then thoroughly wiped and a glass stopper lubricated with Vaseline is inserted, making sure that the ground-glass joint is transparent. The bubble counter is filled with a 50 per cent non-frothing solution of potassium hydroxide by means of a drawn-out glass tube through the open outlet tube so that the tip of the inlet tube will just be immersed in alkali. The outlet tube

is then cleaned inside with a piece of cotton and thoroughly wiped outside. To obtain a non-frothing solution of potassium hydroxide, the solution is shaken with finely ground barium hydroxide (1 g per 200 g of alkali) and then passed through a dry filter.

The other side arm of the drying tube is filled in the following way: first, a dry, loose cotton wad is put into the outlet tube. The tube is closed with a rubber cap and the side arm is filled up to the ground-glass joint, while tapping, with pieces of calcium chloride, which are preliminarily dried in a drier at 180-200 °C. Afterwards, the calcium chloride layer is covered with a piece of dry cotton and the ground-glass joint is wiped, lubricated with Vaseline and closed. The bubble counter is connected to the three-way cock by an artificially aged rubber band.

The drying U-tube is connected to combustion tube 6 by a thick-walled capillary tube, which is linked to the outlet tube of the drier by a piece of vacuum-rubber tubing impregnated with molten Vaseline under vacuum.

Preparation of the Combustion Tube for Operation. Before using the combustion tube, it is washed with a chromic acid mixture and distilled water, then dried. A silver wire 1 mm thick is put into its tapering end through its wide part; one end of the wire should protrude, while the other should be coiled in the tube. The silver spiral prevents water from condensing in the tube owing to high heat conductivity. Afterwards, a layer of silver wool 2 mm thick and a plug of freshly ignited asbestos wool about 5 mm thick are put in. The plug reduces the rate of gas flow through the tube. The asbestos is packed by copper wire.

A layer of fine cupric oxide is put on top of the asbestos plug; in this case, the tube is held vertically and the cupric oxide layer is packed by tapping the tube sides with the palm. The cupric oxide layer is covered with an asbestos plug, which is put in three portions, and each portion is slightly packed with a glass rod. This plug is needed for preventing the vapours of the unburned substance from getting through the filled tube.

A layer of silver wool 2 cm thick is put on the plug, followed by a loose asbestos plug; a 14 cm layer of cupric oxide is then poured while rotating the tube, followed by lead chromate. This layer is also secured by a loose asbestos plug. Afterwards, the tube is thoroughly cleaned by a large cotton wad.

Filling Absorption Devices. To absorb water and carbon dioxide formed in combustion, use absorption tubes with ground-glass hollow stoppers; in this case, one tube is filled with calcium chloride, and another, with soda asbestos. The stopper of the calcium chloride tube is transformed into a "water bag"; for this purpose, a small opening is made in the bottom of the stopper and a

capillary tube is sealed to it. The "water bag" is intended to trap the condensed water drops.

When filling a clean and dry tube with calcium chloride, the stopper is at first slightly lubricated with Vaseline, leaving its upper part (about 2 mm) unlubricated. The tube is closed with a ground-glass stopper having a capillary tube, a small cotton wad is put on the capillary tube, and a 1 cm layer of coarse-grained calcium chloride is poured in and covered with a small piece of cotton. The tube is then filled with millet-sized pieces of ignited calcium chloride almost up to the ground-glass joint on its opposite end. The layer is secured by a dry piece of cotton and the tube is closed with a ground-glass stopper lubricated with Vaseline.

When filling a clean and dry tube with soda asbestos, first insert a ground-glass stopper, which is lubricated with Vaseline and whose cavity has a piece of cotton. A small cotton wool pad is also put on the stopper, and then the tube is filled to two-thirds of its volume with soda asbestos which is covered by a small piece of cotton, followed by a 0.5 cm layer of calcium chloride (which is usually not too dry), and the layer is closed with a cotton. Afterwards, the tube is packed almost up to the ground-glass joint by millet-sized pieces of calcium chloride dried at 180-200 °C. The layer is secured by a dry cotton wad and the tube is closed with a ground-glass stopper, lubricated with Vaseline.

Absorption tubes are connected to one another by 2 cm vacuum-rubber tubing and to the combustion tube by the same tubing 1.5 cm long.

In this case, the rubber tubings should be preliminarily treated with Vaseline under vacuum to reduce gas diffusion through their walls.

The Mariotte bottle is connected so as to maintain definite and easily changeable reduced pressure in the absorption devices. There is a small calcium chloride tube between the Mariotte bottle and the absorption devices.

ANALYSIS

To exactly determine an increase in weight, the absorption devices must be weighed at the same intervals of time. Each absorption tube is thoroughly wiped at first with moist flannel and then with chamois, and is put on the wire stand of the balance, recording the exact time.

In weighing, first the zero point of the balance is determined. The stopcock is then opened for a short time, the pressure is equalized with atmospheric pressure, and the tube is put on the left-hand balance pan by special forceps. The approximate mass

of the tube is determined in 10 min after it is wiped, and its exact mass, in 15 min.

A substance is weighed in a porcelain boat, while a hygroscopic substance, in a special vessel with a cap (Fig. 6.2). It is expedient to switch on the electric circuit at the beginning of weighing and pass air through the combustion tube at the same rate as during the analysis.

After weighing the absorption devices, rubber tubing 1.5 cm long is put on the outlet tube of the absorption device containing calcium chloride. The other outlet tube is connected to the outlet tube of the absorption device containing soda asbestos. The ends of the side arms are butted. The number of air bubbles which pass in 10 sec is checked by the clock and, if need be, the position of the pressure regulator is changed. The absorption device containing calcium chloride is then connected to the combustion tube, while the tube containing soda asbestos is connected to the calcium

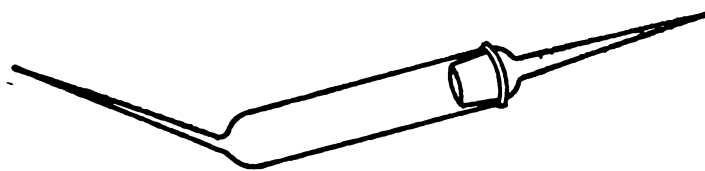


Fig. 6.2. Vessel for weighing hygroscopic substances

chloride tube of the Mariotte bottle. Afterwards, the rubber stopper is taken out of the combustion tube, a boat with a substance is put in, the three-way cock is opened and air is let in. The stopcocks of both the absorption devices and the Mariotte bottle are then opened and combustion is commenced. During an analysis, an eye should be kept on the filling of the gas meter, the bubble counter and the substance.

After passing air through the tube, the stopcocks of both the Mariotte bottle and the absorption devices are closed and the latter are disconnected from the combustion tube. The tube is closed with a rubber cap and allowed to cool. It is then ready for the next analysis. Absorption devices are weighed as indicated earlier. The difference in the mass of absorption devices before and after the analysis shows the amount of water and carbon dioxide that were formed when a substance was being burned.

The percentage of carbon and hydrogen in the test substance is determined by the formulas:

$$C = \frac{b}{a} \times \frac{12.011 \times 100}{44.022}$$

$$H = \frac{c}{a} \times \frac{2.016 \times 100}{18.016}$$

where a = weighed sample of a substance;
 b = amount of CO_2 obtained;
 c = amount of H_2O obtained.

The maximum error of the determination is ± 0.3 per cent for carbon and from $+0.2$ per cent to -0.1 per cent for hydrogen.

6.2. SEMIMICRODETERMINATION OF NITROGEN (ACCORDING TO DUMAS)

The method of determining nitrogen is based on the combustion of a weighed sample of a substance by means of incandescent cupric oxide in a tube filled with carbon dioxide. Free nitrogen is trapped above a potassium hydroxide solution and determined volumetrically.

ASSEMBLY

The apparatus for the semimicrodetermination of nitrogen by the Dumas method consists of the Kipp generator (or Kipp apparatus) for obtaining air-free carbon dioxide, a combustion tube and a semimicronitrometer (Fig. 6.3).

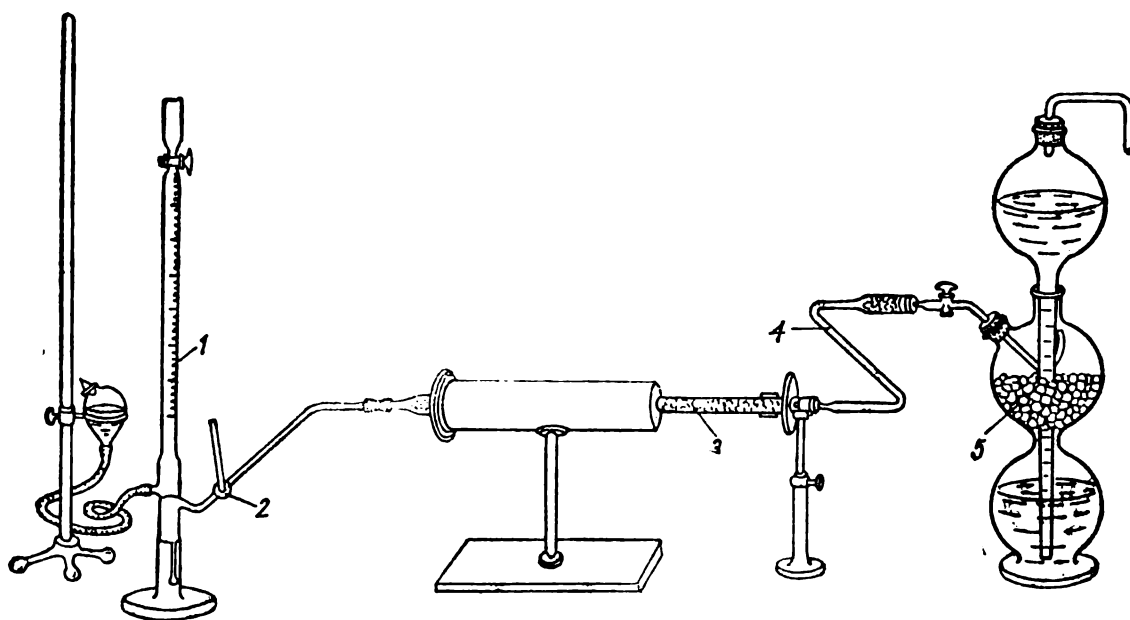


Fig. 6.3. Semimicrodetermination of nitrogen (according to Dumas):
1—semimicronitrometer; 2—regulating cock; 3—combustion tube; 4—Z-shaped glass tube;
5—Kipp generator

Preparation of the Kipp Generator for Obtaining Carbon Dioxide. To determine nitrogen, carbon dioxide completely free of air is needed. Therefore, gases from cylinders cannot be used; it is better to obtain them in the laboratory.

Dilute (1 : 1) hydrochloric acid ($d = 1.18$) is poured over small marble pieces in a porcelain dish. After a vigorous reaction,

slime which has collected on top is poured off and the marble pieces are washed with water and put into the middle globe of the Kipp generator, filling one-half of the globe. A rubber stopper with a glass stopcock is inserted into the tube of the middle globe. A glass tube bent upwards is connected to the stopcock tube in the generator by a short rubber tube so as to remove first the lighter gas impurities. Afterwards, dilute hydrochloric acid is poured into the generator, filling the entire lower globe and half the upper one. Two small marble pieces are then put into the funnel tube, and carbon dioxide which is rapidly liberated forces out air dissolved in the acid.

The newly charged Kipp generator usually gives pure carbon dioxide only after it is allowed to stand for two or three days, when the air absorbed by the glass surface and rubber tubes passes to the carbon dioxide atmosphere. The Kipp generator is connected to the combustion tube by a bent, Z-shaped glass tube. One of its ends that is drawn out into a thick-walled capillary tube is connected to the combustion tube, while the other end, which expands below and is filled with asbestos wool for trapping misty hydrochloric acid, is connected to the stopcock of the Kipp generator.

Preparation of the Combustion Tube. To fill a clean and dry tube with cupric oxide, a small amount of silver wool is put into its drawn-out part, followed by 2-3 mm of asbestos wool as a plug. A layer of coarse cupric oxide 12 cm long is then poured in while tapping the tube sides with the palm, followed by a 6 cm layer of fine cupric oxide and a 10 cm layer of coarse cupric oxide. All this is secured by an asbestos plug.

A hydrogen current which, in order to force out air, has been passed through a bottle containing an acidified solution of potassium permanganate is directed into the filled tube through its wide end. Afterwards, the cupric oxide layer 6 cm thick is reduced by heating it with a burner. The tube is cooled in a slow hydrogen current. The combustion tube is then ignited from end to end in a carbon dioxide current in an electric furnace and allowed to cool under the pressure of carbon dioxide from the Kipp generator.

Filling and Connecting the Semimicronitrometer. The semimicronitrometer is intended for collecting nitrogen which is formed during the combustion of a weighed sample of a substance. It has a 0.02 ml scale division and a capacity of 8-10 ml, corresponding to a 20-30 mg sample of the test substance. The tube through which gas passes into the semimicronitrometer has a glass cock 2 for controlling the gas outflow. The nitrometer is connected to the combustion tube by an obtuse-angled capillary tube. A vacuum-rubber tube, slightly lubricated with glycerol serves as a connection.

Before filling the semimicronitrometer, wash it with a chromic acid mixture and distilled water. The rubber tube which connects the levelling bulb to the semimicronitrometer is fastened with wire. First, pure mercury is poured through the bulb into the nitrometer so that its level is 1-2 mm higher than the opening of the inlet tube. To fill the nitrometer, use a 50 per cent non-frothing potassium hydroxide solution.

The levelling bulb is closed with a rubber stopper which has a short glass tube drawn out into a capillary tube.

ANALYSIS

A small amount of cupric oxide is put into a small test tube having a ground-glass stopper, and then 20-30 mg of a substance are added and everything is weighed. To put a solid test substance into a combustion tube, a feed hopper, which can be made out of a wide test tube, is inserted into it, and a 7 cm layer of coarse and then a 0.5 cm layer of powdered cupric oxide are poured in while tapping the sides of the vertical tube to pack cupric oxide. A 2 cm layer of powdered cupric oxide is added to the weighed sample of a substance that is in the test tube for weighing, the test tube is closed with a cork stopper and shaken, and its contents are poured through the feed hopper into the combustion tube.

The tube is so put into the electric furnace that the cupric oxide layer in the drawn-out part of the tube protrudes from the furnace by 2 cm. To protect this part of the tube from heating, the furnace wall is covered with a small asbestos screen. A sleeve made of a wire net 5 cm long is put on the other end of the tube, and an asbestos screen is placed to protect the rubber stopper from heating. Afterwards, the electric furnace is switched on and the combustion tube is connected to the Kipp generator. Carbon dioxide is passed through the tube for several minutes by opening the stopcock of the generator, and then the combustion tube is connected to the semimicronitrometer, in which alkali should be transferred to the levelling bulb, which is set as low as possible.

Carbon dioxide is allowed to flow for another two minutes, and then the regulating cock of the semimicronitrometer is closed, the latter is filled with alkali, and the levelling bulb is left in a low position. Afterwards, the regulating cock is carefully opened and the carbon dioxide current is so set that 1-2 bubbles per second pass into the nitrometer. As soon as microbubbles begin to pass through the nitrometer, the cock is closed at the Kipp generator and the regulating cock is fully opened. At the same time, a wire sleeve is moved onto the cupric oxide layer, which is at the wide end of the tube, and a burner is applied.

When the electric furnace gets hot in 10-20 min and gases are no longer liberated because the burner has heated the tube, the regulating cock is closed, the levelling bulb is raised above the upper cock of the semimicronitrometer and the cock is turned to and fro, thus letting out the gas which has collected in the nitrometer.

After closing the upper cock of the semimicronitrometer, the levelling bulb is lowered, the regulating cock is opened and the wire sleeve is brought a few millimeters closer to the furnace; in this case, the burner must be on the opposite side of the sleeve. Thus, the sleeve and the burner are moved forward, and it is still seen to it that no more than two gas bubbles get into the nitrometer every three seconds.

As soon as the burner is moved forward to the electric furnace, in 10-25 min, the regulating cock is closed, the stopcock of the Kipp generator is completely opened, and the gas flow rate of two bubbles every three seconds is set again by the regulating cock. The replaceable cupric oxide layer is again strongly heated by a burner through the wire sleeve for 10 min. Afterwards, the burner is turned off and the electric furnace is switched off five minutes later. As soon as microbubbles begin to pass through the semimicronitrometer, the regulating cock is closed and the combustion tube is disconnected and allowed to cool under carbon dioxide pressure.

The semimicronitrometer is left to cool in a cool place; in this case, the levelling bulb should be set at the same level as the liquid in the nitrometer. The nitrogen volume is measured ten minutes later, keeping the meniscus of the levelling bulb on the same level as that of the graduated tube. The reading is taken from the lower end of the meniscus, and then the temperature near the nitrometer and the barometer reading are recorded.

The percentage of nitrogen in the test substance X_N is calculated by the formula:

$$X_N = \frac{1.251V \cdot 273 (P - P_w)}{(273 + t) 760a} \cdot 0.1$$

where 1.251 = mass of 1 ml of pure nitrogen under ordinary conditions, mg;

V = nitrogen volume found, ml;

P = atmospheric pressure, mm Hg;

P_w = pressure of water vapours at a given temperature, mm Hg;

t = temperature, °C;

a = weighed sample of a substance, g.

6.3. MICRODETERMINATION OF CARBON AND HYDROGEN

Quantitative elemental microanalysis of organic substances is widely used. The founder of this method is the Austrian professor, Fritz Pregl. Although very many diverse works have appeared since his day, fundamental changes have not been made in the methodology of determining carbon and hydrogen in organic substances.

A quick method of determination (proposed by M. O. Korshun and V. A. Klimova), which fundamentally differs from the classical method but which is just as reliable, is now widely used in the Soviet Union. In this method, a weighed sample of a test organic substance is burned in a rapid oxygen current in a half-closed region of an empty tube under conditions which ensure long and full contact between a substance, its vapours and decomposition products, on the one hand, and hot oxygen, on the other. In this case, carbon is quantitatively oxidized to carbon dioxide, while hydrogen, to water. If a substance contains the oxidation products of other elements, they are trapped by the appropriate compounds and do not hinder the determination.

Water is absorbed by anhydrous magnesium perchlorate (Anhydron), while carbon dioxide, by the alkali absorber (Ascarite). The absorbed substances are determined by the gain in weight of the absorption devices.

ASSEMBLY

To determine carbon and hydrogen by the micro method, use is made of the apparatus shown in Fig. 6.4. It consists of three main parts: the system for supplying and purifying oxygen, a combustion tube and a system for absorbing combustion products (Fig. 6.5). A detailed description of the individual parts of the apparatus is given below.

System for Supplying and Purifying Oxygen. Oxygen can be supplied from a gas meter or directly from a cylinder. To control the gas flow rate, the cylinder should be fitted out with a precision valve and a manostat (Fig. 6.6). A gas meter can be of any type. The most convenient gas meter consists of two ten-litre bottles which are on one another and are connected by a thick-walled glass tube.

Oxygen in cylinders is usually contaminated and moist; therefore, it should be dried at first by passing it through one or two columns containing drying agents (silica gel, calcium chloride, ascarite). It is best to fill a column with silica gel, impregnated

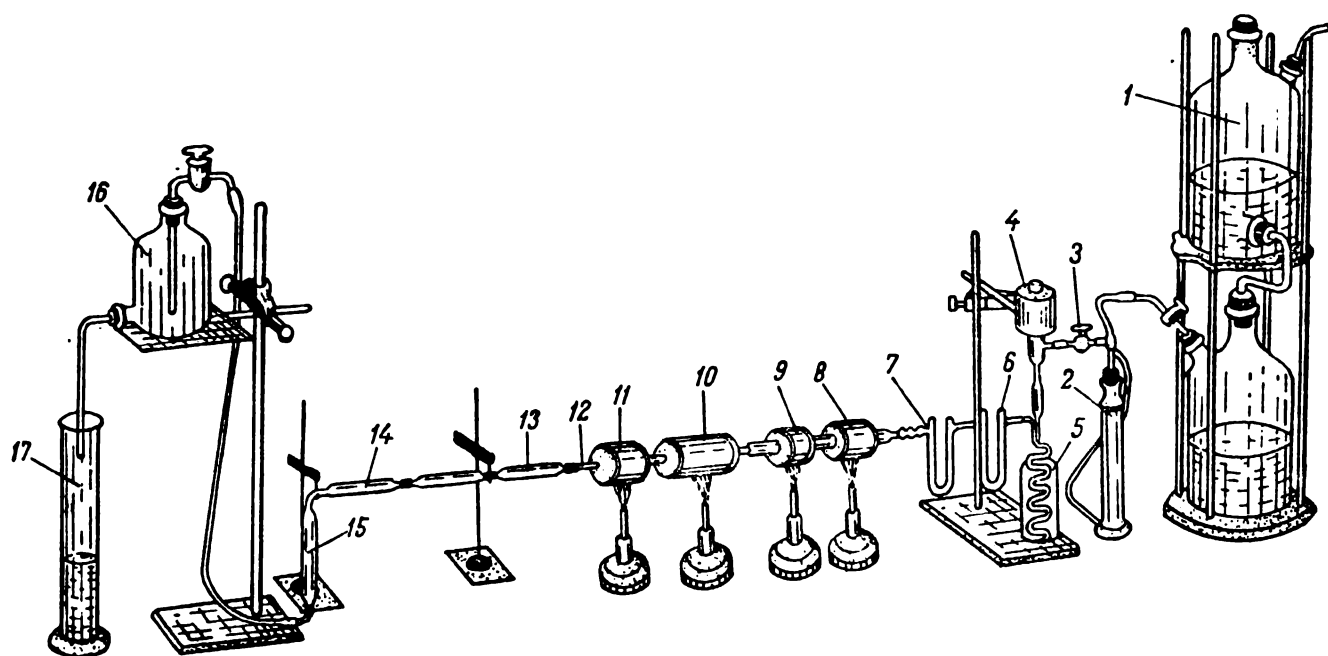


Fig. 6.4. Combustion train for the microdetermination of carbon and hydrogen:

1—gas meter; 2—drying column; 3—stopcock with an incision; 4—catalyst tube; 5—vessel for cooling the coil of the catalyst tube; 6, 7—U-tubes; 8, 9, 10, 11—electric furnaces; 12—narrow part of the combustion tube; 13—water absorption tube; 14—carbon dioxide absorption tube; 15—terminal tube; 16—Mariotte bottle; 17—cylinder

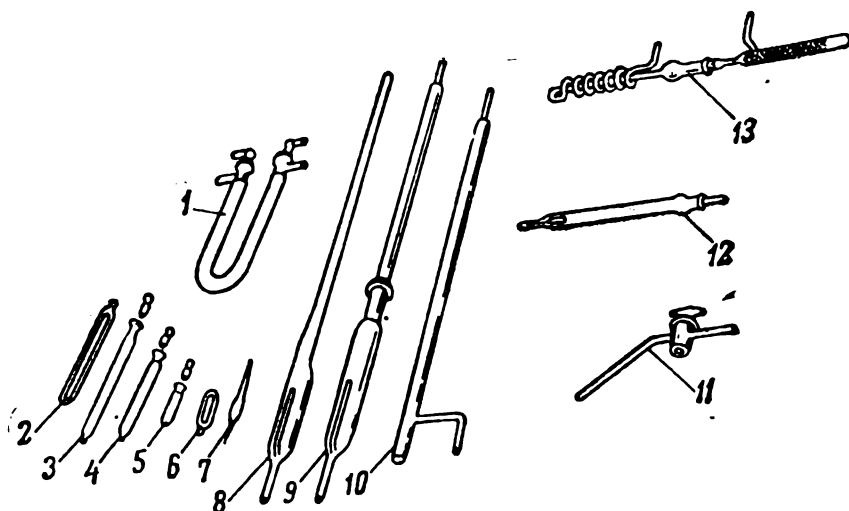


Fig. 6.5. Instruments for the microdetermination of carbon and hydrogen:

1—U-tube; 2, 3, 4, 5, 6, 7—vessels for weighed samples; 8, 9, 10—combustion tubes; 11—stopcock with an incision; 12—absorption tube; 13—catalyst tube

with a cobalt bromide or chloride solution and dried at 210-240 °C. Silica gel having the Soviet code name of KCM or IICM is ground and sifted, and the 0.5-1.0 mm fraction is picked out. The selected silica gel is heated with concentrated hydrochloric acid in a water bath for 2-3 h, washed well with water and dried at 100 °C. It is then heated at 200 °C for 2-3 h.

Dry silica gel (10 parts) is mixed with 20 ml of a 7.5 per cent alcoholic or aqueous solution of cobaltous chloride and again dried at 180-200 °C for 1-2 h. The prepared silica gel is bright blue,

When it absorbs water, it changes colour from blue through violet to pink (depending on the number of moles of water added):

Number of moles of H ₂ O	0	1	1.5	2	4	6
Colour	Blue	Blue-violet	Dark, blue-violet	Pink-violet	Red	Pink

Such a change in colour shows when the silica gel must be changed. The moist preparation is regenerated by drying and heating at 200 °C until it turns blue.

Use can also be made of the silica gel indicator, which is a commercial preparation. It is ground and the 0.5-1.0 mm fraction is picked out and dried at 200 °C.

After drying, oxygen is purified in a catalyst tube; in this case, the impurities of organic substances are oxidized to carbon dioxide

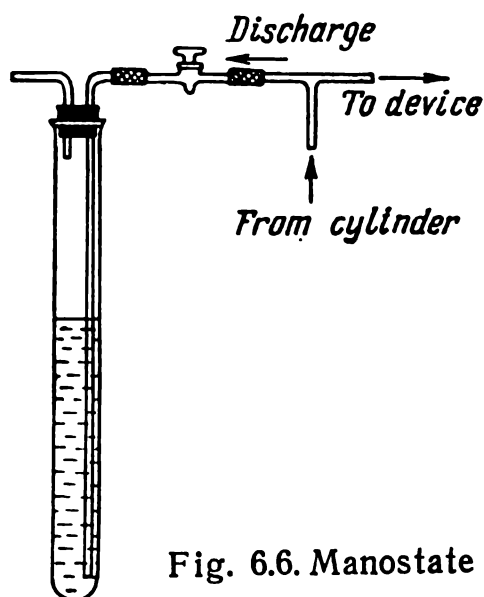


Fig. 6.6. Manostate

and water, which are trapped by Ascarite and Anhydron in U-tubes. To connect the catalyst tube to the drying column, use a vacuum-rubber tube in the middle of which there is a stopcock with an incision for controlling the oxygen flow rate. The comma-like two incisions on the stopcock (Fig. 6.7) are made with a razor.

The catalyst tube (see Fig. 6.5) consists of two parts. The lower part serves as a condenser, while the upper part is filled with cupric oxide and sealed. The tube is filled with cupric oxide in the following way: the side

outlet of the tube is closed with small loose wads of ignited asbestos and cupric oxide is poured until the layer is 1 cm from the top. The unfilled part of the tube is wiped with chamois to remove cupric oxide traces, since they can destroy quartz glass during sealing. The asbestos wad is then taken out of the inner tube and the upper end of the catalyst tube is sealed by a burner in an oxygen current. Afterwards, the upper part is connected to the condenser by Krönig cement. To prepare it, a mixture of one part of beeswax and four parts of colophony are melted in a crucible. The cement becomes soft on heating. It is used to seal the ground-glass joints which are not turned during work.

The catalyst tube usually serves a long time if the cupric oxide layer is not too compact and the temperature of the heater is not higher than 800 °C.*

* When the tube is packed too compactly, it will burst on heating, and when it is heated too strongly, quartz is rapidly destroyed.

The upper part of the catalyst tube, which is filled with cupric oxide, is heated by a vertical-horizontal electric furnace. The catalyst tube is butted to the U-tube by a vacuum-rubber tube.

One-half of the U-tube is filled with Ascarite, and the other half, with Anhydrone, placing Ascarite between two Anhydrone layers. Spacers made of ignited asbestos or glass wool are put between the layers and at the ends of the tube. It is even better to set up two U-tubes; in this case, two-thirds of them are filled with Ascarite, and one-third, with Anhydrone, and they are so arranged that Ascarite is in the middle. For oxygen to have the same moisture when it enters the tube as when it comes out of the device, Anhydrone must be at the end of the entire oxygen purification system.

Combustion Tubes. They are diverse, depending on the method used; in most cases, the flash combustion tube and the pyrolysis combustion tube are employed.

The flash combustion tube consists of two parts which are connected to one another by a ground-glass joint or a rubber tube. The main part of the combustion tube, about 500 mm long, is a wide test tube, in the sealed end of which a narrower tube is inserted. One end of it is bent inward to the test-tube side, while the other end is connected to the oxygen purification system. The sealed end of the test tube serves as a decomposition region. The other part of the combustion tube is straight and has a drawn-out end to which absorption devices are connected. Two furnaces are moved to this part of the tube: a furnace for 950 °C, being an additional oxidation region, and a furnace for 400-600 °C, being a silver heating region which traps halogen and sulphur if they are in the test organic substance. The oxidation region is in the part of the test tube where oxygen enters. This region is heated by a burner flame or a special demountable furnace.

The pyrolysis combustion tube is straight; one of its ends is drawn out, while the other has a side arm whose external diameter is equal to the diameter of the side arms of the U-tubes. Oxygen is fed through the side arm. A furnace for 400-600 °C, which heats silver, is moved to the combustion tube 320 mm away from its drawn-out end, and then the furnace for 950 °C, being the oxidation region, is placed there. The decomposition region is 80 mm away from the side arm, and it can be heated by a burner flame or a demountable furnace.

Filling Absorption Devices. The absorption system consists of several absorption devices, a terminal tube, the Mariotte bottle and a graduated cylinder.

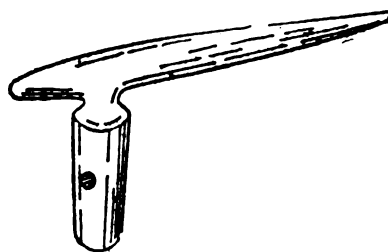


Fig. 6.7. Stopcock with an incision

The water absorption apparatus is filled in the following way: first, a layer of ignited asbestos or glass wool (3-4 mm) is put in. Then Anhydron is poured in while slightly tapping the apparatus, and finally another layer of ignited asbestos or glass wool is put in. The stopper and the ground-glass joint of the apparatus are slightly heated on a small burner flame. The heated stopper is then allowed to touch a lump of Krönig cement 2-3 mm in diameter and the stopper is inserted into the apparatus and turned several times so that the entire ground-glass joint is transparent. If the joint is poorly lubricated, it should be slightly heated, the lubricant removed with a piece of cotton, and everything should be repeated.

The carbon dioxide absorption apparatus is filled in the following way: first, an asbestos wad is put in, then an Anhydron layer (2-2.5 cm) is poured in, followed again by an asbestos wad, Ascarite and an asbestos wad. The ground-glass joint is lubricated and the apparatus is closed as indicated above.

Preparation of the Apparatus for Operation. The U-tube is connected to the catalyst tube and the combustion tube by vacuum-rubber tubing which is 4 cm long and has an inner diameter of 2 mm. To connect the absorption devices to the combustion tube and the terminal tube, use 2 cm vacuum-rubber tubing which has an inner diameter of 1 mm. The inner surface of the rubber tubings are wiped and lubricated with glycerol.

The given temperature in the furnaces is maintained by a rheostat. The gas meter is assembled and its tightness is checked by filling it with oxygen, recording its water level and seeing whether the volume has changed in 2-3 h; the volume should not change.

A drying column is connected to the gas meter, followed by a stopcock with an incision and the catalyst tube, which is placed vertically. The catalyst tube is connected to the U-tube, which is butted to the combustion tube. A furnace is moved to the combustion tube and absorption devices are butted to it. The first to be connected is the device containing Anhydron, and then the device containing Ascarite, and finally the last tube and the Mariotte bottle filled with water. The nose of the bottle is put into the cylinder, and the stopcocks at the gas meter, the stopcock with an incision and the stopcock of the Mariotte bottle are opened. After seeing that oxygen passes through the system, the stopcock of the gas meter is closed and the tightness of the system is checked. When the stopcock of the gas meter is closed, water quickly stops to flow out of the nose of the Mariotte bottle and only drips slightly. When the apparatus is assembled, the oxygen flow rate is set at 25-30 ml/min.

ANALYSIS

To take weighed samples, it is necessary to have boats (see Fig. 6.5), capillary tubes and quartz test tubes. Large quartz test tubes are taken for burning substances which form ash. A weighed sample of volatile liquid compounds is taken in capillary tubes, which are not sealed. Hygroscopic or unstable solid compounds are taken in test tubes having ground-glass stoppers. Small test tubes are used for burning ashless substances.

A sample usually weighs 5-7 mg. Weighed samples of solid substances are taken by a microspatula, which can be made by flattening the tip of an aluminium or copper wire 2-3 mm in diameter with a hammer. Weighed samples of a liquid are taken by a capillary tube, and of viscous liquids, by glass pipettes.

A weighed sample in a boat, in a small test tube and in a capillary tube is put at the sealed end of the combustion tube, i.e., in the decomposition region. (The stopper is removed before putting the test tube into the combustion tube.) It is better to put the capillary tube into the boat. Its open end should be directed towards the sealed end of the combustion tube.

After the weighed sample is put in, combustion is commenced. A furnace is put under the part of the combustion tube into which oxygen enters. Another furnace is put almost directly under the weighed sample. When the part of the tube into which oxygen enters is heated, the furnace is slowly moved to the weighed sample until the substance bursts into flame. After finishing combustion, the furnace is so put that it closes the entire expanded part of the tube. Combustion lasts 2-3 min, and then the furnace is slowly (for 5-7 min) moved along the entire length of the tube to completely drive out the combustion products. The furnace is then removed and the stopcock of the Mariotte bottle is closed. The apparatus are removed, wiped and weighed on the semimicroanalytical balance.

Check weighings must be made from time to time. The correction used in calculations is determined by the results of the analysis of a check substance.

Calculation. Correction n (mg) is calculated by the formulas:

$$n_{\text{CO}_2} = a - \frac{Ag}{M}, \quad n_{\text{H}_2\text{O}} = b \frac{Bg}{M}$$

where a = gain in weight of CO_2 , mg;

A = mass of CO_2 calculated by a reaction when a gram molecule of a check substance was being oxidized, g;

g = weighed sample, mg;

M = molecular weight of the check substance;

b = gain in weight of H_2O , mg;

B = mass of H_2O calculated by a reaction when a gram molecule of the check compound was being oxidized, g.

The percentage of carbon and hydrogen is calculated by the formulas:

$$X_{\text{C}} = K_{\text{CO}_2} \times 100 \frac{a - n_{\text{CO}_2}}{g} \quad X_{\text{H}} = K_{\text{H}_2\text{O}} \times 100 \frac{b - n_{\text{H}_2\text{O}}}{g}$$

where

$$K_{\text{CO}_2} = \frac{M_{\text{C}}}{M_{\text{CO}_2}} = \frac{12.01}{44.01} = 0.2729 \quad K_{\text{H}_2\text{O}} = \frac{M_{\text{H}_2}}{M_{\text{H}_2\text{O}}} = \frac{2.016}{18.016} = 0.1119$$

Example. Check substance: saccharose $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, $M = 342.31$. Sample weighs 6.325 mg; yield: CO_2 9.800 mg; H_2O 3.750 mg.

Theoretically, 6.325 mg of saccharose gives (mg):

$$\text{CO}_2 = \frac{44.01 \times 12}{342.31} \times 6.325 = 9.758$$

$$\text{H}_2\text{O} = \frac{18.016 \times 11}{342.31} \times 6.325 = 3.662$$

Calculation of the correction (mg):

$$n_{\text{CO}_2} = 9.800 - 9.758 = 0.042$$

$$n_{\text{H}_2\text{O}} = 3.750 - 3.662 = 0.088$$

Sample weighs 5.280 mg; yield: CO_2 8.180 mg; H_2O 3.150 mg.

The percentage of carbon and hydrogen with regard to the correction is:

$$X_{\text{C}} = 0.2729 \times 100 \frac{8.180 - 0.042}{5.280} = 42.05$$

$$X_{\text{H}} = 0.1119 \times 100 \frac{3.150 - 0.088}{5.280} = 6.49$$

Part II

SYNTHESES OF ORGANIC SUBSTANCES

Chapter 7

HALOGENATION REACTIONS

Halogen-containing organic compounds are widely used as solvents, antiseptics, narcotics, insecticides, plant growth stimulators, coolants, medicinals, monomers in polymer production and as initial substances in the production of various organic substances. Halogen derivatives of hydrocarbons are widely used in various syntheses because their halogen atom is capable of being replaced by different groups (amino, carboxyl, hydroxyl and others).

The following methods of introducing a halogen atom into the molecules of an organic substance are of the greatest importance:

- (1) the replacement of the hydroxyl group in alcohols and acids, and also of the oxygen atom in aldehydes and ketones, by a halogen;
- (2) the addition of a halogen and a hydrohalide by the multiple bond;
- (3) the direct replacement of hydrogen by a halogen.

7.1. REPLACEMENT OF THE HYDROXYL GROUP OF ALCOHOLS BY A HALOGEN

To replace the hydroxyl group in alcohol by a halogen, use reagents which contain atoms or atomic groups capable of binding the hydroxyl group. In most cases, such a replacement is achieved under the action of hydrohalic acids (HCl, HBr, HI), halogen compounds of phosphorus (PI₃, PBr₃, PCl₅), and thionyl chloride or bromide (SOCl₂, SOBr₂). Alcohols react most readily with hydriodic acid, which is commonly used for obtaining iodine derivatives of higher alcohols. The reaction with hydrochloric acid occurs with the greatest difficulty, and when primary alcohols are used, it is necessary to add a dehydrating agent, such as anhydrous zinc

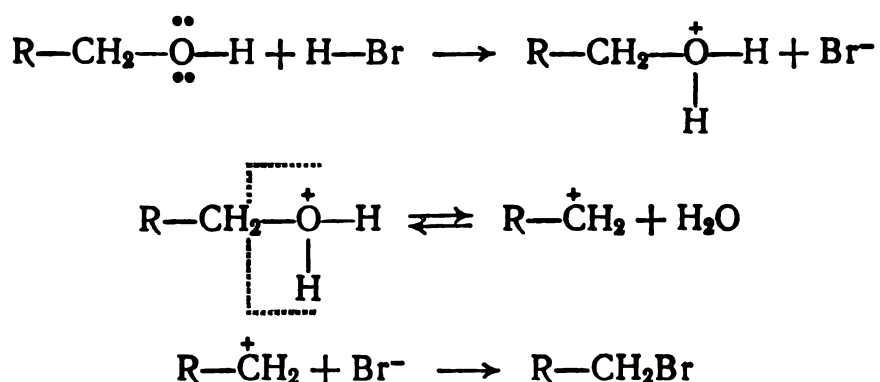
chloride. Alcohols which react most intensively are tertiary alcohols (it is enough to mix alcohol with a concentrated aqueous solution of hydrohalic acid), and those which react with the greatest difficulty are primary alcohols. The action of hydrohalic acids on alcohols can be represented by the following equations:



where X is a halogen (Cl, Br, I).

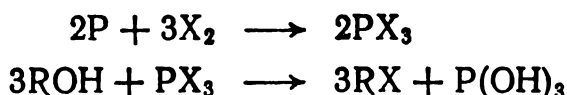
This reaction is reversible, because the halogen derivative obtained is decomposed by water into initial substances. If the reaction is to continue to the end, water or alkyl halide should be removed from the reaction mixture. Therefore, in order to obtain a halogen derivative, it is most convenient to use not hydrohalic acid, but its salt and concentrated sulphuric acid (at the moment of formation, hydrohalic acid acts more intensively). This method can be employed to obtain, for instance, the bromides of methyl, ethyl, butyl, etc.

The following represents the reaction mechanism of the formation of halogen derivatives from alcohols and hydrohalides:



There is also a method of synthesizing two halogen derivatives simultaneously, e.g., when bromine acts on a readily brominating hydrocarbon in the presence of primary alcohol. This method can be used to obtain α -bromonaphthalene and ethyl bromide, α -bromonaphthalene and methyl bromide, α -bromonaphthalene and propyl bromide, etc.

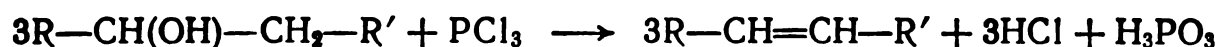
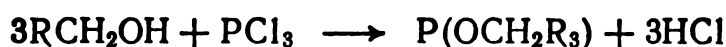
The hydroxyl group in alcohol can be replaced by a halogen also under the action of phosphorus trihalide and pentahalide. Phosphorus trihalides commonly used are PBr_3 and PI_3 . They react, in this case, with alcohols at the moment of their formation from phosphorus and a halogen:



where X is iodine or bromine.

In most cases, iodine derivatives are obtained by this method. The application of phosphorus trichloride is limited. It is used only

in chlorinating tertiary alcohols and phenols because its reaction with primary alcohols gives phosphites, and with secondary alcohols, unsaturated hydrocarbons:



The phosphorus pentahalides used are PCl_5 and PBr_5 , which react with alcohols in the following way:



The interaction between phosphorus pentachloride and alcohols (primary, secondary and tertiary) is the most widely used method for obtaining chlorine derivatives from alcohols. The phosphoryl chloride (POCl_3) formed also reacts with alcohols on heating:



Thionyl chloride (SOCl_2) is also used for this purpose:



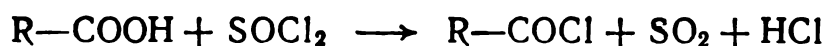
7.2. REPLACEMENT OF THE HYDROXYL GROUP OF ACIDS BY A HALOGEN

Acid halides are formed when the hydroxyl group in acids is replaced by a halogen. Phosphorus halides and thionyl chloride or bromide (SOCl_2 , SOBr_2) are used to obtain them.

Among acid halides, acid chlorides are widely used because the chlorine atom is very mobile. To obtain acid chlorides, use is made mainly of phosphorus trichloride, thionyl chloride and phosphorus pentachloride:



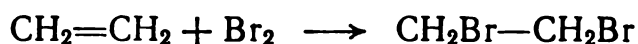
The selection of a reagent depends on many factors, such as the boiling point of an acid chloride and the readiness with which an acid reacts. The technique of separating an acid chloride from by-products, however, is important; therefore, it is convenient to use thionyl chloride, which gives only the gaseous, readily water-soluble products SO_2 and HCl :



Phosphorus trichloride is used for obtaining acid chlorides of lower acids, and phosphorus pentachloride, for obtaining acid chlorides of higher acids. Acid bromides are obtained like acid chlorides, i.e., with the employment of phosphorus bromide compounds. Acid iodides are obtained under the action of an iodine and phosphorus mixture on acids.

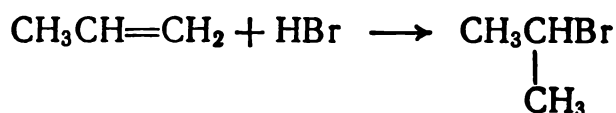
7.3. HALOGEN ADDITION BY THE MULTIPLE BOND

Unsaturated hydrocarbons are capable of adding halogens to the double and triple bonds. In the laboratory, the bromination of ethylene hydrocarbons is used most often; dibromo derivatives with bromine atoms at the adjacent carbon atoms are then obtained:



The reaction of bromine addition to unsaturated hydrocarbons is widely used in organic synthesis for detecting and quantitatively determining ethylene and acetylene bonds. The amount of bromine (in grams) that is added to 100 g of an organic substance is known as the bromine number. The rate at which a halogen is added to unsaturated hydrocarbons depends on the hydrocarbon structure, the catalyst, the temperature, and other factors.

HCl, HBr and HI are added by the multiple bond with the formation of alkyl monohalogen, e.g.,

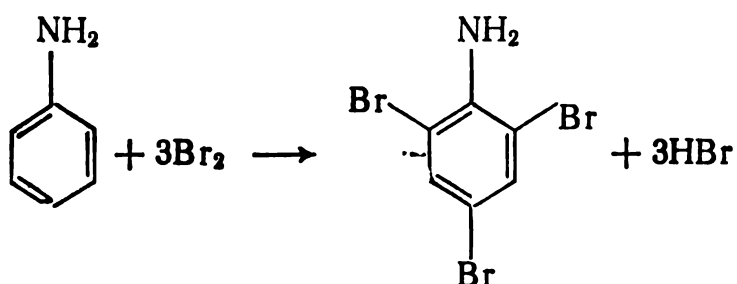


7.4. DIRECT REPLACEMENT OF HYDROGEN BY A HALOGEN

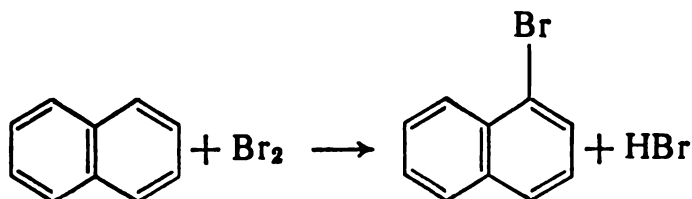
A mixture of various products is often obtained in the reactions of the direct replacement of the hydrogen atoms by a halogen. In this case, several hydrogen atoms are consecutively replaced with the formation of a mixture of mono-, di- and trihalogen derivatives and an isomeric mixture. It is difficult to separate the mixtures obtained because the components have similar boiling points. Therefore, the direct substitution reaction is convenient only in rare instances when a hydrogen atom in the molecule of the initial substance is far more readily capable of being replaced by a halogen than the others, i.e., when a hydrogen atom is in the α -position of the electron-acceptor group. It follows that carboxylic acids, aldehydes, ketones and ethers of the fatty series are readily halogenated.

The reaction of the direct replacement of hydrogen by a halogen is widely used also in synthesizing the halogen derivatives of the aromatic series. The direct replacement of hydrogen by a halogen largely depends on temperature, light and the catalyst (iron, aluminium salt, phosphorus, iodine, etc.). When the appropriate catalyst and temperature are selected, the required product is obtained in a large amount even in the light. In conformity with these conditions, hydrogen can be replaced by a halogen in either the side chain or the benzene ring. In the side chain, the replacement

occurs on heating and under the action of light without a catalyst (e.g., in obtaining benzyl chloride from toluene). In the presence of a catalyst, replacement occurs in the aromatic ring (e.g., when obtaining bromobenzene in the presence of iron). The replacement of hydrogen by a halogen in the aromatic ring is affected also by the presence of the hydroxyl or the amino group in the ring, as they increase the mobility of hydrogen atoms in the *o*- and *p*-positions. For instance, when bromine water acts on aniline, three hydrogen atoms of the benzene ring are readily replaced by bromine atoms, as a result of which symmetrical tribromoaniline is formed:



alpha-Bromonaphthalene is easily obtained when a substitution reaction is carried out in an organic solvent (acetic acid or carbon tetrachloride):



A halogen is bonded more firmly with the benzene or naphthalene ring when the bond is direct rather than when it is from the side chain.

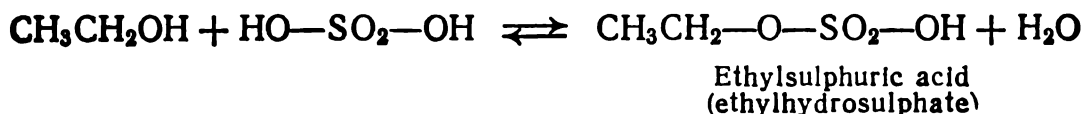
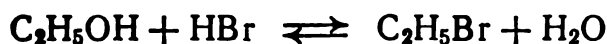
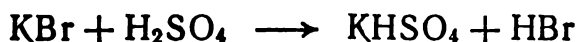
7.5. SYNTHESSES

ETHYL BROMIDE

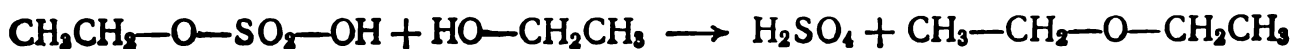
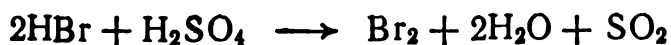
Formula:



Main reactions (for the reaction mechanism, see p. 124):



Side reactions:



Reagents and Equipment

Ethyl alcohol, 95 per cent	28 ml	Flasks, round-bottom (100 and 300 ml)	2
	(0.5 mole)	Flask, conical (200 ml)	1
Potassium bromide	30 g	Funnel, separatory	1
	(0.25 mole)	Funnel, dropping	1
Sulphuric acid ($d = 1.84$)	33 ml	Condenser, Liebig	1
	(0.6 mole)	Dephlegmator	1
		Thermometer	1
		Adapter, bent	1

Assembly

1. A 300-ml round-bottom flask is put into a sand bath and fitted to a dephlegmator and a long condenser, to which a bent adapter is connected. The end of the adapter is immersed by 1-1.5 cm in a mixture of water and ice in a receiver put in an ice bath (Fig. 7.1).

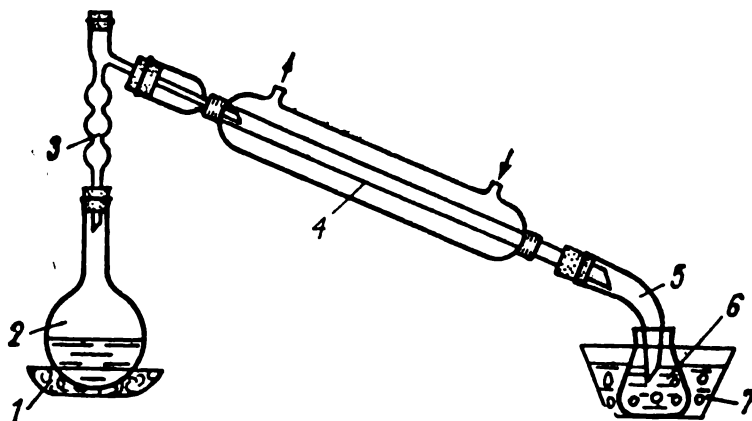


Fig. 7.1. Apparatus for obtaining ethyl bromide:

1—sand bath; 2—round-bottom flask; 3—dephlegmator; 4—condenser; 5—bent adapter; 6—receiver; 7—ice bath

Since ethyl bromide is volatile, the distillate is collected in a receiver containing water and several pieces of ice so as to reduce losses.

2. A 100-ml round-bottom flask is immersed in a water bath and boiling stones are put into it. The flask is fitted with a dephlegmator having a thermometer and a water condenser with a bent adapter which is put into the receiver that is cooled on the outside by ice. Since ethyl bromide boils at a low temperature (38-39 °C), use is made of a condenser (the longer the better), through which a strong jet of cold water is passed.

Procedure

In a 300-ml reaction flask, 28 ml of ethyl alcohol are mixed with 20 ml of cold water, which is added in order to reduce the formation of the by-product (ethyl ether), lessen the losses of the very volatile hydrobromic acid, and partially dilute sulphuric acid

to preclude the redox reaction of bromine formation. To make fuller use of the hydrobromic acid being formed, alcohol is taken in excess.

While continuously stirring the reaction mixture and cooling the flask by running water 33 ml of sulphuric acid and then 30 g of finely ground potassium bromide are carefully added. Apparatus 1 is assembled and the reaction mixture is heated by a large flame in a sand bath. Ethyl bromide which collects under the water-and-ice layer soon begins to be driven off. If the reaction mixture in the flask foams, heating is reduced for a short time.

The reaction mixture is heated until ethyl bromide, which does not dissolve in water no longer drips from the condenser. Distillation is so carried on that the oily drops of ethyl bromide continuously enter the receiver while the liquid in the receiver does not rise into the condenser.

In distillation, water in the receiver is occasionally sucked back into the bent adapter. In this case, lower the receiver so as to free the end of the adapter. When all the water has dripped into the receiver, the adapter is put back in the initial position.

After the reaction, the contents of the receiver are poured into the separatory funnel, the heavy (lower) layer of ethyl bromide is separated into a 200-ml conical flask, which is put into a vessel containing finely crushed ice, and while gently shaking the flask, concentrated sulphuric acid is added to it dropwise until the liquid separates into layers.

The ethyl bromide is washed with sulphuric acid to remove ethyl ether, which is obtained as a by-product in the reaction. Sulphuric acid acts, in this case, also as a dehydrating agent which dries ethyl bromide. Since heat is liberated (and this can cause a loss of highly volatile ethyl bromide), the flask is always kept in a cooling bath (finely crushed ice).

The contents of the flask are transferred to a separatory funnel and the lower sulphuric-acid layer is separated. Crude ethyl bromide dried by sulphuric acid is distilled off from a 100-ml round-bottom flask (apparatus 2).

The crude ethyl bromide is yellow, indicating that dissolved bromine impurities are present in it. The yield of ethyl bromide is 22 g.

Ethyl bromide (bromoethane) is a colourless liquid with an ethereal odour; 0.914 g of it dissolves in 100 g of water at 20 °C (this should be taken into account and the receiver should not contain much water). It dissolves well in alcohol and ether, and possesses properties which are typical of the halogen derivatives of saturated hydrocarbons. It turns yellow in the light owing to the liberation of free bromide. Its molecular weight is

108.98; m.p., -119 °C; b.p., 38.3 °C; d_4^{20} , 1.4586, and n_D^{20} , 1.4211.

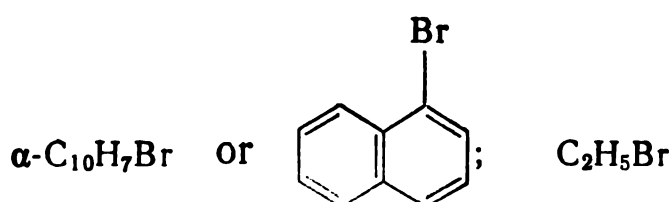
It is employed as a narcotic and a coolant. It is also used with CH_3Cl and $\text{C}_2\text{H}_5\text{Cl}$ for obtaining ethylbenzene and ethylmalonic ether, in Grignard's synthesis, and for inhalation.

Highly concentrated ethyl bromide affects the nervous system. It is stored in sealed ampoules or in thick-walled bottles with a ground-glass stopper.

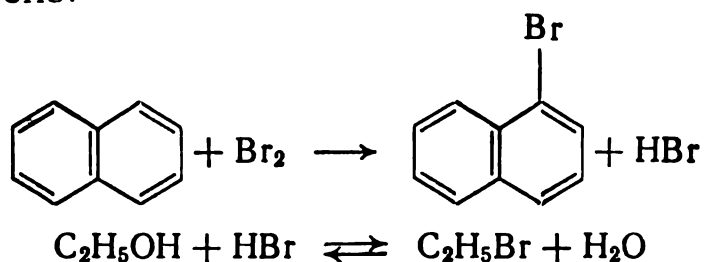
Characterization Test. When a copper wire wetted with ethyl bromide is put in a flame, the flame becomes bright green because a volatile compound of copper and bromine is formed. This flame colour is characteristic of halogen derivatives (Beilstein test).

α -BROMONAPHTHALENE AND ETHYL BROMIDE

Formulas:



Main reactions:



Reagents and Equipment

Naphthalene	16 g (0.12 mole)	Flask, round-bottom, wide-mouth, (250 ml)	1
Ethyl alcohol, 95 per cent	8 ml (0.14 mole)	Flask, round-bottom (50 ml)	1
Bromine	8 ml (0.16 mole)	Flask, conical (100 ml)	1
		Adapter, three-mouth	1
		Dephlegmator	1
		Funnel, dropping	1
		Funnel, separatory	1
		Condenser, Liebig	1
		Adapter, bent	1
		Apparatus, superheated steam distil- lation	1
		Apparatus, vacuum distillation	1

Assembly

1. A 250-ml round-bottom, wide-mouth flask is put in a water bath and closed with a stopper having a three-mouth adapter. A stopper with a tube is selected beforehand for the reaction flask in order to distil α -bromonaphthalene with superheated steam. A stirrer is put in the straight neck of the adapter. A dropping funnel and a small dephlegmator connected to the Liebig condenser are put in the two other necks. A bent adapter is connected to the

condenser, and its end is immersed by 1-1.5 cm in water with ice in a conical flask (Fig. 7.2).

2. Apparatus 2 on page 128 (in this case, a 50-ml round-bottom flask is used).

3. Superheated steam distillation apparatus (see Figs. 3.6 and 3.7).

4. Apparatus for vacuum distillation from the Claisen flask (see Fig. 3.9).

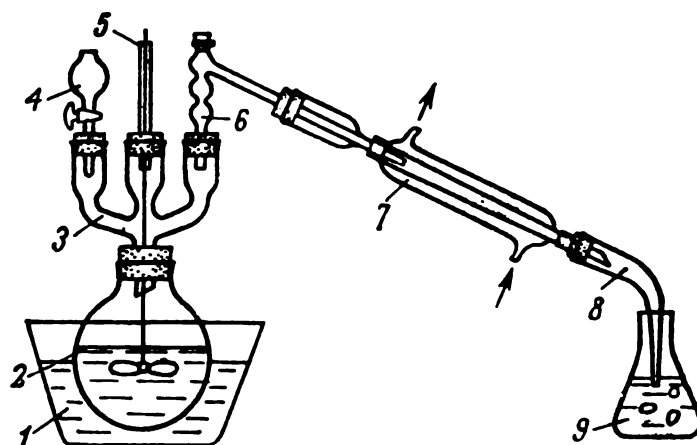


Fig. 7.2. Apparatus for obtaining α -bromonaphthalene and ethyl bromide: 1—water bath; 2—round-bottom wide-mouth flask; 3—three-mouth adapter; 4—dropping funnel; 5—stirrer; 6—dephlegmator; 7—condenser; 8—bent adapter; 9—receiver

Procedure

Sixteen grams of finely ground naphthalene are put into a 250-ml round-bottom, wide-mouth flask which is set up in conformity with the description of apparatus 1, and then 8 ml of ethyl alcohol are poured in. The contents of the flask are stirred and carefully heated to 40-50°C in a water bath. While continuously stirring the reaction mixture, 8 ml of bromine are added to it from a dropping funnel (see p. 15) at such a rate that the temperature of the mixture will be no higher than 50°C.

When methyl or propyl alcohol is added to the reaction mixture, α -bromonaphthalene and methyl bromide or α -bromonaphthalene and propyl bromide are obtained, respectively. When bromine is put in the reaction mixture, the temperature at which the corresponding alkyl bromide boils should be maintained.

After all the bromine has been put in the flask, the water bath is heated to 60°C. Heating should always be controlled so as to prevent the contents of the flask from foaming. The reaction mixture is heated until the oily drops of ethyl bromide, which sink to the bottom of the receiver, no longer drip into it.

After the reaction, ethyl bromide is separated from water in a separatory funnel and discharged into a conical flask. To dry ethyl bromide and free it from alcoholic impurities, the flask is put

into a vessel containing ice and then concentrated sulphuric acid is added dropwise from a dropping funnel while shaking the flask (see p. 15). As soon as the liquid separates into layers, it is poured into a separatory funnel. The sulphuric-acid layer, which collects beneath, is separated from ethyl bromide, while the latter (see p. 129) is transferred to a 50-ml distilling flask and distilled in a water bath (apparatus 2) at 35-40 °C. The yield of ethyl bromide is about 5 g.

In the 250-ml round-bottom flask, the residue is a mixture of α -bromonaphthalene, unreacted naphthalene and a small amount of hydrobromic acid. Naphthalene, hydrobromic acid and a small amount of α -bromonaphthalene are removed in distillation with steam superheated to 130 °C.

To prevent some α -bromonaphthalene from being lost, it is separated from water, put back in the reaction flask and redistilled with steam. When naphthalene crystals no longer appear in the condenser the flask is cooled, α -bromonaphthalene (lower layer) is separated from water in a separatory funnel and dried by calcium chloride.

Dried α -bromonaphthalene is distilled under vacuum from the Claisen flask at 132-135 °C and a residual pressure of 12 mm Hg (first fraction), and at 145-148 °C and a residual pressure of 20 mm Hg (second fraction).

α -Bromonaphthalene distilled under atmospheric pressure darkens on storage because it partially decomposes. Its yield is about 13 g.

α -Bromonaphthalene is a yellowish liquid with a characteristic odour. It is water-insoluble and mixes with alcohol, ether and gasoline. Its molecular weight is 207.07; b. p., 281.2 °C; m. p., 6.1 °C; d_4^{15} , 1.4883; and n_D^{15} , 1.6600.

It is used as a heat carrier in driers and for determining the refractive index of minerals, synthesizing α -naphthoic acid and other purposes.

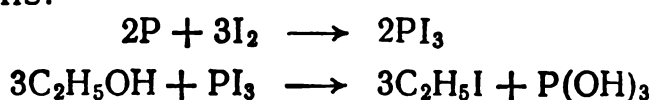
Characterization Test. α -Bromonaphthalene gives the Beilstein reaction for halogens (see p. 130).

ETHYL IODIDE

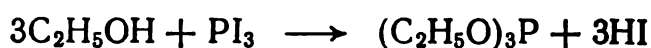
Formula:



Main reactions:

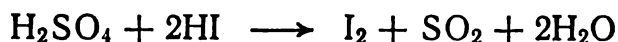


Side reaction:



Ethyl iodide cannot be obtained under the action of potassium iodide and sulphuric acid on alcohol because the hydriodic acid

formed reduces sulphuric acid to sulphur dioxide:



Therefore, to obtain ethyl iodide, use phosphorus triiodide, which is formed when iodine and phosphorus react. Hydriodic acid, unlike hydrobromic acid, often reduces sulphuric acid to free sulphur.

Reagents and Equipment

Ethyl alcohol, absolute . . . 17 ml	Flask, round-bottom (100 ml) 1
(0.3 mole)	Flask, Würtz (50 ml) 1
Iodine 32 g	Flask, conical (50 ml) 1
(0.25 gram atom)	Head, still 1
Red phosphorus 3.1 g	Funnel, separatory 1
(0.1 gram atom)	Thermometer 1
Acid sodium sulphite	Adapter, bent 1
	Receiver 1

Assembly

1. A still head adapter is inserted in a 100-ml round-bottom flask which is in a water bath, and its vertical branch is closed with a rubber stopper, while its side arm is connected to a reflux water condenser.

2. A 100-ml reaction flask is connected by a bent glass tube to a downflow condenser, at the end of which there is a bent adapter that is lowered almost to the bottom of the receiver cooled by cold water from the outside.

3. Boiling stones are put in a 50-ml Würtz flask, a thermometer is inserted, and the flask is connected to a downflow condenser with a bent adapter, which is lowered into the receiver.

Procedure

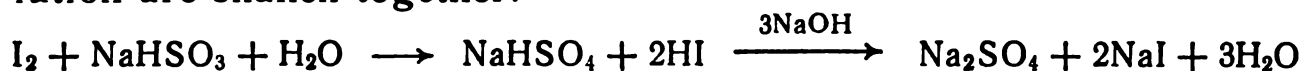
Work should be done *in a fume cupboard!* As much as 3.1 g of red phosphorus, dried in a desiccator over sulphuric acid, are put in the reaction flask of apparatus 1 assembled in the fume cupboard, and 17 ml of absolute ethyl alcohol are added. (To make fuller use of expensive iodine, the amounts of phosphorus and alcohol taken are more than those theoretically required.)

Thirty-two grams of iodine, finely ground in a mortar, are weighed out. After placing the reaction flask into ice water and fitting the reflux condenser, iodine is put in the flask in small portions through the vertical neck of the still head adapter for 10-15 min. Whenever a portion is added, the flask is tightly stoppered and shaken well.

The reaction mixture is then allowed to stand for one hour while shaking the flask now and then. The mixture is heated in a hot water bath for two hours. The reaction flask is then cooled and

connected to the downflow condenser (apparatus 2), and ethyl iodide is driven off while heating the flask in a boiling water bath. The flask is taken out of the water bath, wiped with a towel and since ethyl iodide is driven off very slowly at the end of distillation, the ethyl iodide residue is driven off by continuously passing a small smoky burner flame around the flask.

The distillate obtained contains a certain amount of alcohol and is brown owing to the iodine impurity. The distillate is transferred to a separatory funnel and the upper water layer is separated. The ethyl iodide is then washed with water two or three times to remove ethyl alcohol. To remove iodine, about 1 ml of an acid sodium sulphite solution is added to the last portion of water. Finally, to neutralize full decoloration, ethyl iodide and a dilute alkaline solution are shaken together:



The lower layer is poured into a 50-ml conical flask, dried by granulated calcium chloride and distilled from the Würtz flask (apparatus 3), and the fraction which boils at 72-72.3 °C is collected. If calcium chloride floats on the surface of ethyl iodide, alkyl halide is poured through the funnel containing glass wool. The yield of ethyl iodide is about 30 g.

Ethyl iodide (iodoethane) is a heavy colourless liquid which dissolves sparingly in water; its d_4^{20} is 1.9371; n_D^{20} , 1.5168, and b. p., 72.3 °C. It is used for obtaining phenetole, ethylbenzene and ethylmalonic acid. It is stored in a well-stoppered dark bottle.

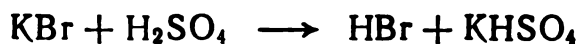
BUTYL BROMIDE

Formula:

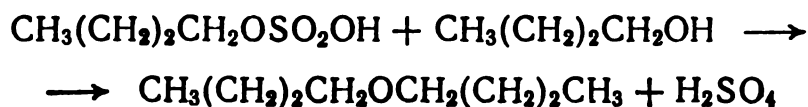
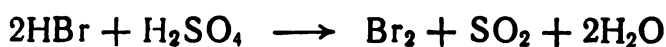
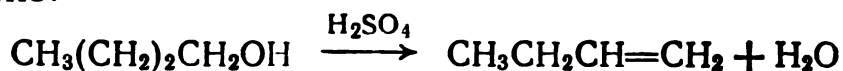


Preparation of Butyl Bromide Using Potassium Bromide

Main reactions:



Side reactions:



Reagents and Equipment

Butyl alcohol	28 ml (0.32 mole)	Flask, round-bottom (300 ml) . .	1
Potassium bromide	30 g (0.25 mole)	Flask, Würtz (50 ml)	1
Sodium hydroxide, 10 per cent	20 ml	Condenser, Liebig	1
Calcium chloride	5 g	Funnel, conical	1
Sulphuric acid ($d = 1.84$) . .	23 ml (0.43 mole)	Funnel, separatory	1
Acid sodium sulphite		Gauze, asbestos	1
		Receivers	2

Assembly

1. A few boiling stones are put in a 300-ml round-bottom flask, which is connected to a water reflux condenser. The condenser is loosely secured in a ring stand (this is necessary because the flask is shaken during stirring).

2. Apparatus 2 on page 128 (in this case, a 300-ml round-bottom flask is used).

3. Apparatus 3 on page 133.

Procedure

Thirty millilitres of water and 28 ml of butyl alcohol are poured into the round-bottom flask of apparatus 1 and 30 g of potassium bromide are added. The flask is cooled from the outside by running water and 23 ml of concentrated sulphuric acid are slowly added while mixing well by shaking the flask. The contents of the flask are heated to boiling by a small flame on an asbestos gauze for two hours. Apparatus 2 is then assembled and butyl bromide, which contains impurities of water, butyl ether, butylene, butyl alcohol and bromine, is rapidly driven off.

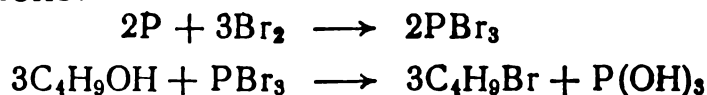
The distillate is transferred to a separatory funnel, washed with 20 ml of water containing a small amount of acid sodium sulphite for eliminating the colour caused by the presence of bromine traces, and the lower layer of butyl bromide is poured into a clean flask. The separatory funnel is washed and dried, butyl bromide is transferred to it, and an equal volume of concentrated sulphuric acid is added to it (provided the flask is cooled outside) so as to remove butyl ether. Two layers are then formed: the upper butyl bromide layer and the lower sulphuric acid layer. The layers are separated and butyl bromide is washed with 20 ml of a 10 per cent sodium hydroxide solution (so as to remove sulphuric acid traces). Turbid butyl bromide is dried by five grams of calcium chloride while being slightly heated in a water bath.

As soon as the contents of the flask become clear, dried butyl bromide is poured into a 50-ml Würtz flask and distilled and the

fraction which boils at 99-103°C is collected. The yield of butyl bromide is about 23 g.

Preparation of Butyl Bromide by Bromine and Red Phosphorus

Main reactions:



Reagents and Equipment

Butyl alcohol	19 g or 23.5 ml (0.25 mole)	Flasks, round-bottom (100 and 250 ml)	2
Red phosphorus	3.9 g (ca. 0.12 gram atom)	Flask, conical	1
Bromine	31.4 g or 10 ml (ca. 0.2 mole)	Head, still	1
Acid sodium sulphite		Condenser, Liebig	1
Calcium chloride		Funnel, conical	1
		Funnel, dropping	1
		Funnel, separatory	1
		Apparatus, steam distillation	1
		Dephlegmator	1
		Receivers	2

Assembly

1. A 250-ml round-bottom flask is placed in a cooling bath and boiling stones are put in it. A stopper with two tubes, which will be needed for subsequent steam distillation, is selected beforehand for the flask.

The flask is fitted with a still head having a reflux condenser and a dropping funnel. The clamp of the condenser stand is loose so that the flask can be shaken better.

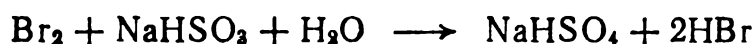
2. Steam distillation apparatus (see Fig. 3.6). To prevent some butyl bromide from being lost, use a long, well-cooled condenser.

3. Boiling stones are put into a 100-ml round-bottom flask, which is connected to a dephlegmator fitted with a thermometer and with a Liebig condenser having a bent adapter lowered into the receiver.

Procedure

Work should be done *in a fume cupboard!* Put 3.9 g of red phosphorus dried in a desiccator over sulphuric acid and 23.5 ml of butyl alcohol in a round-bottom flask of apparatus 1. The flask is cooled and 10 ml of bromine are slowly added (in the course of one hour) from a dropping funnel while frequently shaking the flask (see Chap. 1). After all the bromine has been put in, the reaction mass is heated for three hours in a water bath until bromine vapours disappear. The contents of the flask should boil vigorously. After the reaction, butyl bromide is driven off with steam from

the same reaction flask. The distillate is transferred to a separatory funnel and shaken with a 10 per cent acid sodium sulphite solution so as to remove bromine traces:



The lower layer of butyl bromide is poured into a clean flask and dried by granulated calcium chloride until the contents of the flask become clear. Dried butyl bromide is poured through a funnel with glass wool into a 100-ml round-bottom flask and distilled off (apparatus 3). The fraction which boils at 99-103 °C is collected. The yield of butyl bromide is about 28 g.

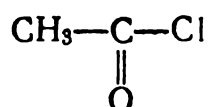
Butyl bromide is a colourless liquid which dissolves well in alcohol and ether. Its molecular weight is 137.03; b.p., 101.6 °C; m.p., -112.4 °C; d_4^{20} , 1.2829; and n_D^{20} , 1.4398.

It is used as an alkylating agent, as well as in nitrile synthesis.

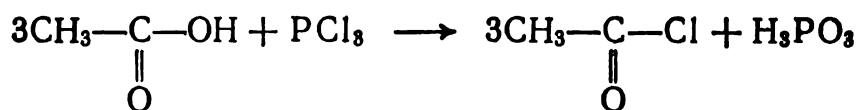
Characterization Test. Butyl bromide gives the Beilstein reaction for halogens (see p. 130).

ACETYL CHLORIDE

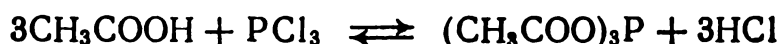
Formula:



Main reaction:



Side reaction:



Reagents and Equipment

Acetic acid, glacial . . .	23 g or 22 ml (0.38 mole)	Flask, round-bottom (200 ml) . . .	1
Phosphorus trichloride	18 g or 11 ml (0.13 mole)	Flask, Würtz (200 ml)	1
Calcium chloride		Condenser, Liebig	1
		Funnel, dropping	1
		Flask, conical (100 ml)	1
		Dephlegmator	1
		Tubes, calcium chloride	2
		Thermometer	1
		Adapter, bent with side arm . . .	1

Assembly

1. A 200-ml Würtz flask placed in a water bath is connected to a dropping funnel and a Liebig condenser. The inner tube of the condenser is connected to a conical flask by a bent adapter which has a calcium chloride tube (Fig. 7.3).

Acetyl chloride is readily decomposed by moisture, and therefore it should not be collected in an open receiver.

2. A 200-ml round-bottom flask placed in a water bath is connected to a dephlegmator, a thermometer and a Liebig condenser having a bent adapter. The adapter has a side arm on which the calcium chloride tube is put on. The adapter is connected to the receiver through a stopper.

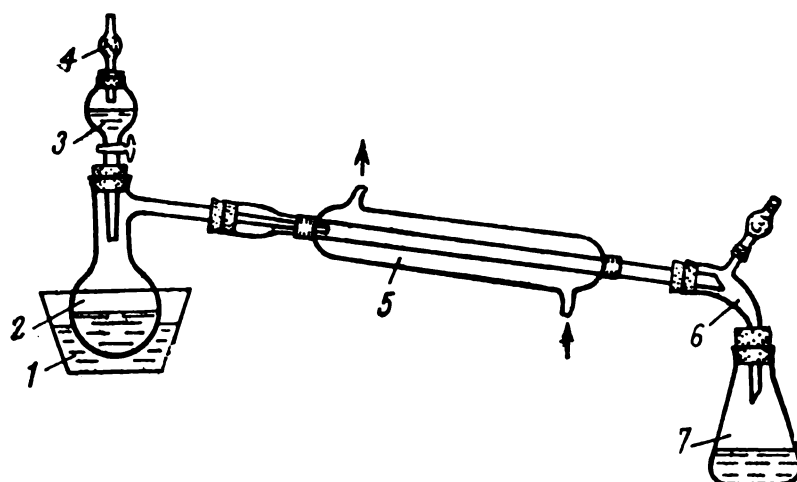


Fig. 7.3. Apparatus for obtaining acetyl chloride:

1—water bath; 2—Würtlz flask; 3—dropping funnel; 4—calcium chloride tube; 5—condense ; 6—bent adapter with a calcium chloride tube; 7—receiver

Procedure

Work should be done *in a fume cupboard!* Twenty-two millilitres of glacial acetic acid are put in the flask of apparatus 1 (**caution:** glacial acetic acid is highly flammable and forms explosive mixtures with air; its vapours act on the mucous membranes and the skin; if the acid gets on the skin, the affected place should be washed with much water). The flask is placed in a cold water bath. Eleven millilitres of phosphorus trichloride are gradually poured through a dropping funnel into the flask, which is shaken from time to time. After all the phosphorus trichloride has been put in, the reaction mixture is heated for 30 min in a water bath at 40-50 °C. Continue heating until hydrogen chloride is no longer vigorously liberated and two layers have formed in the liquid. Acetyl chloride forms the upper layer, while phosphorous acid, the lower one. The water bath is heated until it boils and acetyl chloride is driven off.

To completely purify the distillate, it is redistilled (apparatus 2). Acetyl chloride is collected at 50-53 °C. Its yield is about 18 g.

Acetyl chloride (ethanoyl chloride) is a colourless, water-insoluble liquid which fumes in air and has a pungent odour; it dissolves well in organic

solvents. Its molecular weight is 78.54; b. p., 51.8 °C; m. p., -112 °C; d_4^{20} , 1.1051; and n_D^{20} , 1.3897.

It is used in acetylation and for producing dyes and medicinals as well as for other purposes.

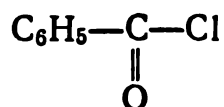
Characterization Tests. 1. Acetyl chloride gives the Beilstein reaction for halogens (see p. 130).

2. It fumes in air, undergoing hydrolysis under the action of humidity.

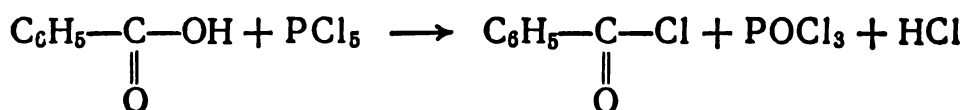
3. Acetyl chloride is hydrolyzed when it is shaken with water. The solution obtained gives an acid reaction for congo red.

BENZOYL CHLORIDE

Formula:



Main reaction:



Reagents and Equipment

Benzoic acid	12.2 g (0.1 mole)	Flask, round-bottom (100 ml) . . .	1
Phosphorus pentachloride	21 g (0.1 mole)	Flask, Würtz (100 ml)	1
		Flask, conical	1
		Condenser, air	1
		Condenser, Liebig	1

Assembly

1. A 100-ml round-bottom flask is connected by a rubber stopper to a reflux air condenser.

2. A 100-ml Würtz flask is connected to a thermometer and a Liebig condenser.

Procedure

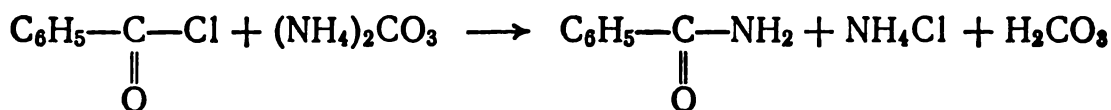
Work should be done *in a fume cupboard!* Put 12.2 g of benzoic acid and 21 g of phosphorus pentachloride in a round-bottom flask (apparatus 1). The flask is then shaken until the mixture becomes a liquid.

Apparatus 2 is assembled. First, phosphoryl chloride is driven off at 110 °C, and then, after replacing the water condenser by an air condenser, benzoyl chloride is distilled off at 199 °C. The yield of benzoyl chloride is about 10 g.

Benzoyl chloride is a colourless liquid which fumes slightly in air and has a pungent odour. It dissolves well in ether, chloroform and benzene. Its molecular weight is 140.57; b. p., 197.9 °C; m. p., -0.6 °C; d_4^{20} , 1.219; and n_D^{20} , 1.5535.

Benzoyl chloride is used for detecting alcohols, amines and phenols, and for synthetic purposes. It is stored in bottles closed well with ground-glass stoppers or in ampoules. Benzoyl chloride vapours irritate the mucous membranes, causing lachrymation.

Characterization Test. A benzamide precipitate is formed when two grams of ammonium carbonate are ground with one gram of benzoyl chloride in a porcelain dish:

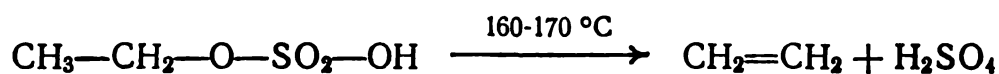
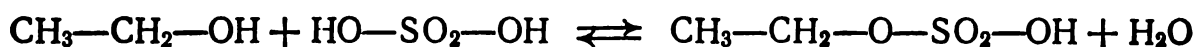


1,2-DIBROMOETHANE

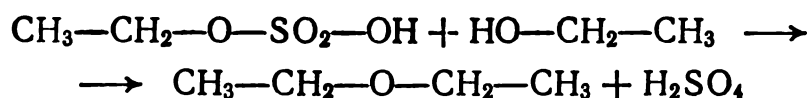
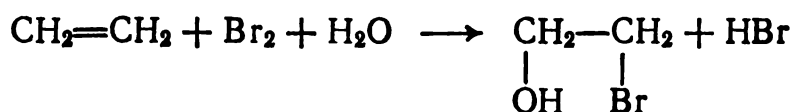
Formula:



Main reactions:



Side reactions:



Reagents and Equipment

Ethyl alcohol, 95 per cent	45 ml	Flask, round-bottom (500 ml) . . .	1
	(0.7 mole)	Flask, Würtz (100 ml)	1
Bromine	31.4 g or 10 ml	Flasks, conical	2
	(0.2 mole)	Condenser, Liebig	1
Sulphuric acid ($d = 1.84$)	90 ml	Funnel, dropping	1
	(1.7 moles)	Thermometer	1
Aluminium sulphate, anhydrous	10 g	Bottles, Drexel	3
Sodium hydroxide		Bottle, Tishchenko	1
Calcium chloride		Beakers	3
Sand, dry coarse-grained		T-piece	1
		Adapter, bent	1

Assembly

1. A 500-ml round-bottom flask is placed in a sand bath. The opening of the flask is tightly closed with a stopper which has a long-stem dropping funnel, a thermometer and a right-angled gas tube. The gas outlet tube is connected to the Drexel wash bottle, which contains concentrated sulphuric acid (for purifying ethylene from the vapours of alcohol and ether). The bottle is placed in a

beaker containing cold water. The wash bottle is cooled from the outside to prevent ethylene from being lost since at elevated temperature ethylene reacts with sulphuric acid, forming ethylsulphuric acid.

The wash bottle is connected by a T-piece to the Tishchenko bottle, which contains 4 *N* sodium hydroxide solution used for purifying ethylene from sulphur dioxide. The T-piece is connected by a bent tube to the upper opening of the dropping funnel in order to equalize pressure in the apparatus.

Pressure should be equalized; otherwise, ethylene will not pass through sulphuric acid. It will go instead through the dropping funnel because the weight of the liquid column in the funnel will

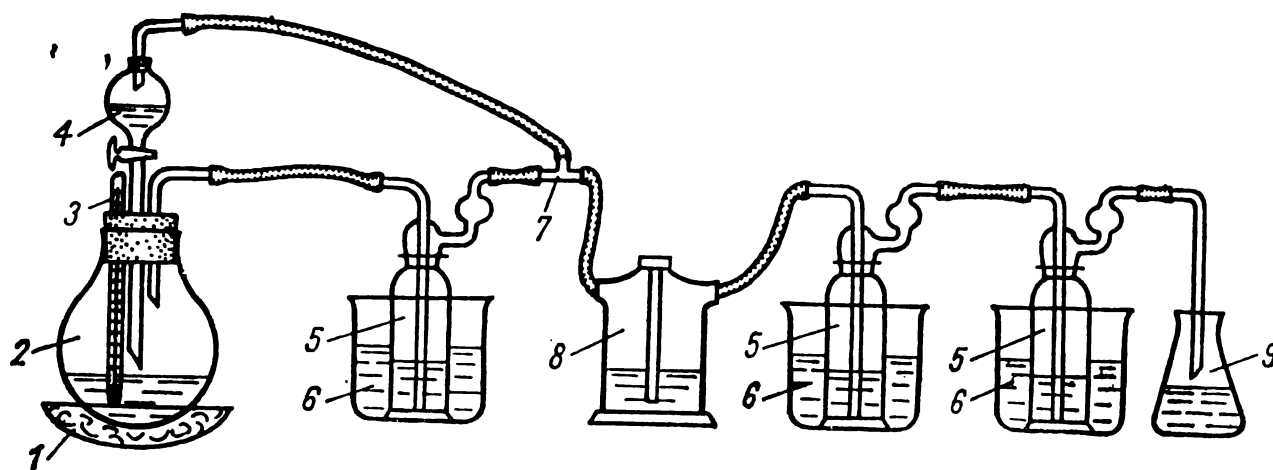


Fig. 7.4. Apparatus for obtaining 1,2-dibromoethane:

1—sand bath; 2—round-bottom flask; 3—thermometer; 4—dropping funnel; 5—Drexel bottle; 6—beaker; 7—T-piece; 8—Tishchenko bottle; 9—conical flask

be less than the total weight of the liquid column in the wash bottles.

The Tishchenko safety bottle is connected to two Drexel absorption bottles that are filled with bromine and placed in beakers containing cold water, which is changed during a reaction (the bottles must be cooled because the bromine-ethylene combination reaction evolves heat). The outlet tube of the last Drexel bottle is lowered into a conical flask containing 2 *N* sodium hydroxide solution (for absorbing bromine vapours which volatilize from bromine-containing bottles) without immersing the tube in the liquid. To check whether bromine completely absorbs ethylene, the tube is immersed from time to time by 0.5 cm in a sodium hydroxide solution. If the reaction is being carried out correctly, ethylene will rarely bubble out of the tube.

Before commencing work, it is necessary to see whether the apparatus (Fig. 7.4) is correctly assembled and make sure the absorption bottles are gas-proof. To do the latter, a wash bottle containing sulphuric acid is connected to the absorption bottles

and to a gas meter filled with nitrogen or air. An eye is kept on the gas bubbles when nitrogen is passed through the absorption system.

2. A 100-ml Würtz flask is connected to a thermometer and a Liebig condenser having a bent adapter, which is lowered into a 50-ml conical flask.

Procedure

Fifteen millilitres of ethyl alcohol are poured into a round-bottom flask of apparatus 1 and 45 ml of concentrated sulphuric acid are carefully added while stirring and cooling the flask from the outside. Afterwards, 20 g of dry coarse-grained sand from which fine particles have been sifted off (to accelerate water elimination) and 10 g of anhydrous aluminium sulphate which acts catalytically are put in. A mixture of 30 ml of ethyl alcohol and 45 ml of concentrated sulphuric acid are then put in the dropping funnel. In this case, the tube of the dropping funnel must be filled up with a mixture of alcohol and sulphuric acid. Before putting the funnel in the flask, its stopcock is opened and its outlet tube is immersed in a mixture of alcohol and sulphuric acid. The mixture is carefully sucked in until the outlet tube is filled up. The stopcock is then quickly closed, the flask is stoppered, and the remaining mixture is poured into the dropping funnel.

The flask is so heated in a sand bath that the temperature does not rise higher than 170 °C. A mixture of alcohol and sulphuric acid is gradually poured in from the dropping funnel. The rate at which the mixture is added should be so controlled that ethylene will be evolved rapidly (but not in a continuous stream) and the mass being heated will not greatly foam in the flask. The ethylene evolved passes through the Drexel wash bottle containing concentrated sulphuric acid, the Tishchenko bottle containing 4 *N* sodium hydroxide solution and two Drexel absorption bottles each containing 5 ml of bromine with a 1 cm layer of water on top (in order to reduce bromine losses due to evaporation).

When bromine colour disappears in both absorption bottles two hours after the beginning of the reaction, the bottles are immediately disconnected, otherwise, their content may mix on cooling.

Crude dibromoethane is transferred to a separatory flask and washed with water and then with a dilute sodium hydroxide solution until it is decolourized, and again with water several times. The product is dried over calcium chloride and distilled (apparatus 2) at 130-132 °C. The yield of 1,2-dibromoethane is about 30 g.

1,2-Dibromoethane is a colourless liquid which dissolves well in organic solvents. Its molecular weight is 187.89; b.p., 131.5 °C; m.p., 9.97 °C; d_4^{20} , 2.1806; and n_D^{20} , 1.5380. It is poisonous and affects the skin.

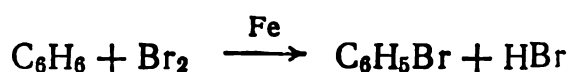
It is used for obtaining ethylene diamine and synthesizing medicinals, e.g., piperazine, and as an additive to motor fuel.

BROMOBENZENE

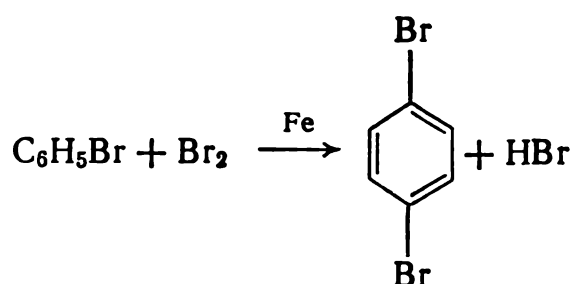
Formula:



Main reaction:

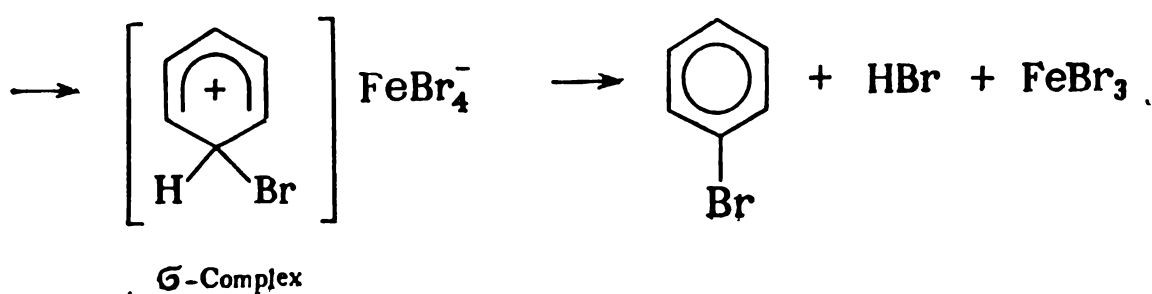
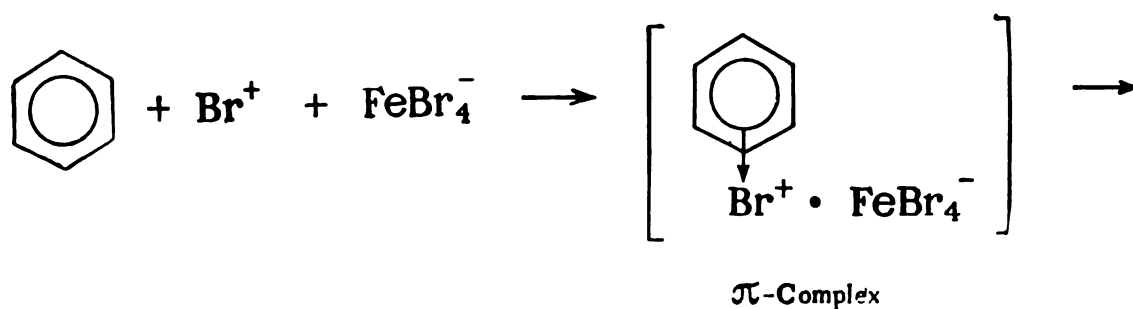
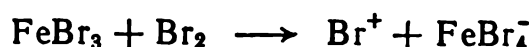
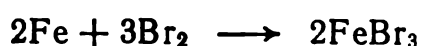


Side reaction:

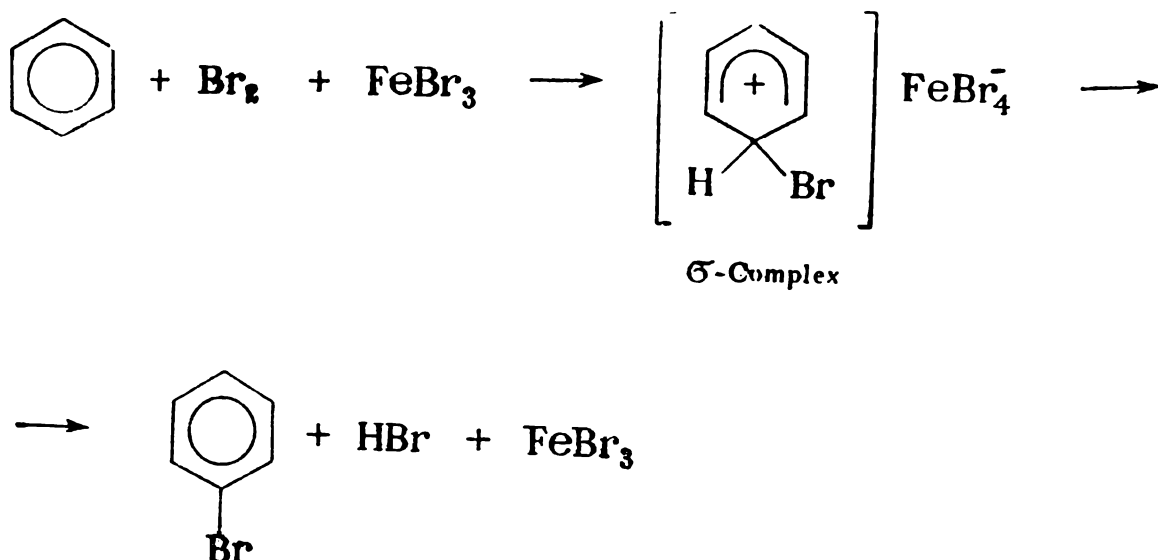


Benzene is brominated in the presence of a catalyst (iron); there can be two mechanisms:

(a) with the preliminary ionization of bromine



(b) without preliminary ionization

**Reagents and Equipment**

Benzene	19.4 g or 22 ml (0.25 mole)	Flask, round-bottom (200 ml)	1
Bromine	31.4 g or 10 ml (0.2 mole)	Flask, Würtz (50 ml)	1
Iron filings	0.5 g	Head, still	1
Calcium chloride	12 g	Condenser, Liebig	1
		Condenser, air	1
		Funnel, dropping	1
		Funnel, conical	1
		Funnel, separatory	1
		Apparatus, steam distillation	1
		Dish, porcelain	1
		Beaker	1
		Adapter, bent	1
		Thermometer	1
		Receivers	2

**Preparation of Bromobenzene
by Steam Distillation****Assembly**

1. A 200-ml round-bottom flask is connected by a still head adapter to a dropping funnel and a reflux water condenser.

The reaction yield largely depends on the correct assembly and tightness of the apparatus. Bromine corrodes rubber and cork stoppers. The purest reaction product is therefore obtained when an apparatus with ground-glass joints is used. If cork stoppers are used, they should be treated with paraffin, and if rubber ones are used, they should be slightly lubricated with Vaseline (see Chap. 1).

A bent glass tube is inserted in the upper end of the condenser and connected by rubber tubing to an inverted glass funnel, which is placed in a beaker over the surface of cold water in order to absorb the hydrogen bromide formed in the reaction. The funnel

should be 1-2 cm away from the water surface. The apparatus (Fig. 7.5) should be put in a *fume cupboard*!

2. Steam distillation apparatus (see Fig. 3.6).

3. A thermometer is inserted in a 50-ml Würtz flask, which is connected to the air condenser with a bent adapter at its end.

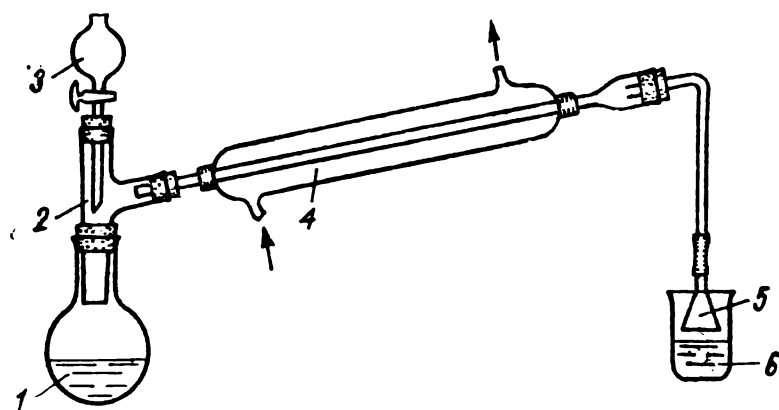


Fig. 7.5. Apparatus for obtaining bromobenzene:

1—round-bottom flask; 2—still head adapter; 3—dropping funnel; 4—condenser; 5—funnel; 6—beaker with water

Procedure

Iron filings in an amount of 0.5 g are put in a 200-ml reaction flask and 22 ml of benzene, preliminarily dried over calcium chloride, are added. Bromine is then slowly poured in from the dropping funnel while shaking the flask (see Chap. 1). The reaction begins immediately if the bromine, benzene and the vessels are all dried well. If the reaction is delayed, the mixture can be slightly heated in a water bath. When hydrogen bromide begins to be liberated, residual bromine is so poured in that the reaction occurs uniformly and intensively, but does not become vigorous, because dibromobenzene can be formed when bromine is introduced rapidly and the temperature is raised.

When all the bromine is introduced, the contents of the flask are heated for 20-30 min in a water bath to complete the reaction, and the temperature is gradually raised from 15-25 °C to 60-70 °C until the brown bromine vapours over the liquid disappear. Water is then poured into the flask, the mixture obtained is shaken and the solution is carefully poured from the flask into the separatory funnel while making sure that the iron filings do not get into the funnel. The liquid is again washed with water and distilled with steam (apparatus 2). At first, bromobenzene is distilled off, when *p*-dibromobenzene crystals appear in the condenser, the receiver is changed and *p*-dibromobenzene is collected until only water condenses. Bromobenzene which has been driven off is separated from water in a separatory funnel, dried over calcium chloride for one hour and distilled from a 50-ml Würtz flask by an air condenser (apparatus 3).

To dry bromobenzene, it is put, together with calcium chloride, into a flask fitted with a reflux air condenser. The mixture is heated in a water bath to 60-70 °C (while frequently shaking it) until the liquid in the flask becomes clear.

The fraction which boils at 140-170 °C is obtained; the remaining liquid is poured from the Würtz flask into a porcelain dish, and when it solidifies, it is added to *p*-dibromobenzene, which is obtained by steam distillation.

The *p*-dibromobenzene precipitate is dried on filter paper (to remove liquid *o*-dibromobenzene) and recrystallized from a small amount of alcohol (see p. 59).

The fraction which boils at 140-170 °C is redistilled (apparatus 3) and pure bromobenzene is collected at 152-158 °C. The yield of bromobenzene is about 14 g.

Preparation of Bromobenzene by Simple Distillation

Assembly

1. Apparatus for obtaining bromobenzene (see Fig. 7.5).
2. Apparatus 3 on page 145 for obtaining bromobenzene.

Procedure

Bromination is carried out as in the previous case. The product obtained is transferred to a separatory funnel, washed with water, poured into a dry flask, dried by calcined calcium chloride and distilled (apparatus 2). The fraction which boils at 140-170 °C is collected. This fraction is redistilled at 154-160 °C. The residue in the Würtz flask is treated in the same way as indicated on page 146. The yield of bromobenzene is about 13 g, and that of *p*-dibromobenzene, about 1 g.

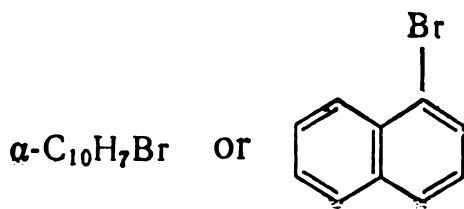
Bromobenzene is a heavy clear liquid with an odour similar to that of benzene, it is sparingly soluble in water and well soluble in alcohol, ether, chloroform and benzene. Its molecular weight is 157.02; b. p., 156.2 °C; m. p., -30.6 °C; d_4^{20} , 1.495; and n_D^{20} , 1.5602.

It is used in Grignard and Fittig reactions, as a heat carrier for driers, and for other purposes.

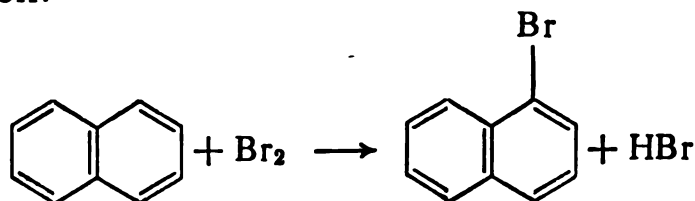
p-Dibromobenzene consists of colourless crystals which melt at 89 °C; it is well soluble in alcohol and ether, and sparingly soluble in water. It is used as an intermediate in syntheses.

α -BROMONAPHTHALENE

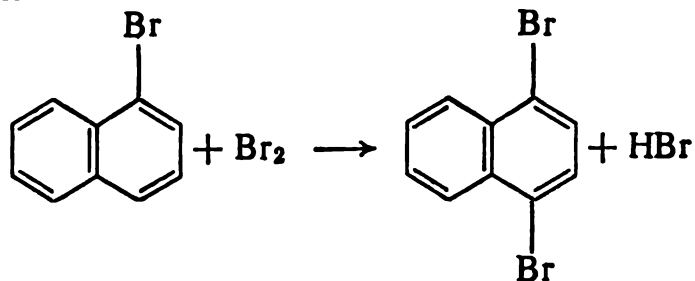
Formula:



Main reaction:



Side reaction:



1,4-Dibromonaphthalene

Reagents and Equipment

Naphthalene	25.6 g (0.2 mole)	Beaker (200 ml)	1
Bromine	31.4 g or 10 ml (0.2 mole)	Apparatus, superheated steam distillation	1
Calcium chloride		Apparatus, vacuum distillation . .	1
		Funnel, dropping	1
		Funnel, separatory	1
		Thermometer	1

Assembly

1. A 200-ml beaker is put in a water bath. A thermometer and a dropping funnel whose tube almost reaches the bottom of the beaker are secured in a ring stand.
2. Superheated steam distillation apparatus (see Figs. 3.6 and 3.7).
3. Vacuum distillation apparatus (see Fig. 3.9).

Procedure

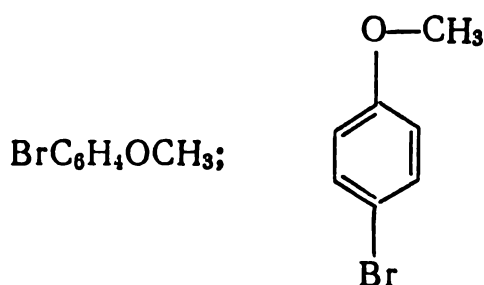
Work should be done *in a fume cupboard!*. Put 25.6 g of finely ground naphthalene and 40 ml of water in a 200-ml beaker and, while stirring and heating the mixture in a water bath to 40-50 °C, 10 ml of bromine are added dropwise from the dropping funnel so that the temperature of the reaction mixture is not higher than 50 °C. After all the bromine is added, stirring is continued until the yellow colour of the reaction mass disappears. The contents of the flask are then transferred to a separatory funnel and the lower oily layer is separated from the water layer. The oil is then transferred to a 250-ml flask and distilled with steam superheated to 130 °C (apparatus 2) so as to remove unchanged naphthalene and other impurities from α -bromonaphthalene, about 70-80 ml of the liquid should be driven off. Steam distillation is continued until naphthalene crystals in the condenser disappear. The oil which

remains in the reaction flask is dried by calcium chloride and distilled under vacuum from the Claisen flask (apparatus 3). The fraction which boils at 145-148 °C (20 mm Hg) or 132-135 °C (12 mm Hg) is collected. The yield of α -bromonaphthalene is about 20 g (see p. 132).

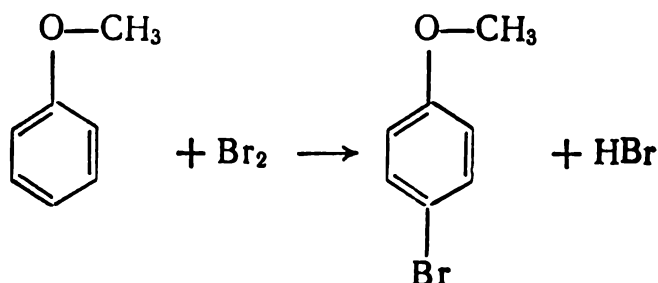
α -Bromonaphthalene can be synthesized in a three-necked flask fitted with a thermometer, a dropping funnel and a reflux condenser, which is connected to a bent glass tube lowered into a water-containing beaker in a way that it is slightly above the water surface. In this case, hydrogen bromide is trapped.

p-BROMOANISOLE

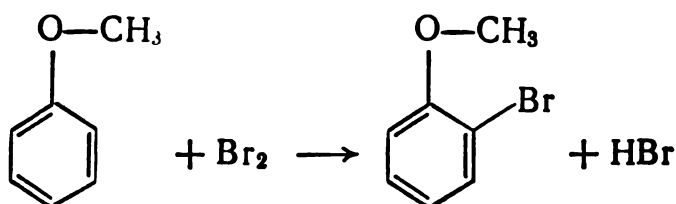
Formula:



Main reaction:



Side reaction:



Reagents and Equipment

Anisole	14.5 g or 14.6 ml (ca. 0.13 mole)	Flask, Würtz (150 ml)	1
Bromine	22 g or 7 ml (ca. 0.14 mole)	Flask, round-bottom (200 ml)	1
Ethyl ether	70 ml	Flask, conical	1
Calcium chloride, anhydrous		Head, still	1
		Condenser, Liebig	1
		Funnel, dropping	1
		Funnel, separatory	1
		Thermometer	1
		Condenser, air	1

Assembly

1. Apparatus for obtaining bromobenzene (see Fig. 7.5).
2. Würtz flask with a thermometer and a Liebig condenser.

Procedure

Put 14.6 ml of anisole in a 200-ml reaction flask, which is slightly heated, and slowly add 7 ml of bromine through a dropping funnel (see Chap. 1). After all the bromine is added, the mixture is heated for 15 min and then cooled, and 70 ml of ether are added. The ethereal solution is washed with water in a separatory funnel and dried by anhydrous calcium chloride. Ether is driven off in a water bath (apparatus 2), and then the water condenser is replaced by an air condenser and *p*-bromoanisole is collected at 213-223 °C.

The yield of *p*-bromoanisole is about 15 g. *p*-Bromoanisole is obtained with the *o*-bromoanisole impurity, which is difficult to remove, because both isomers have similar boiling points.

p-Bromoanisole is a heavy liquid with a pleasant odour. Its b.p. is 213-223 °C; m.p., 11.5 °C, and n_D^{20} , 1.5605.

Chapter 8

ALKYLATION REACTIONS

Alkylation is the introduction of alkyl radicals (methyl, ethyl, propyl, butyl, amyl, etc.) into organic compounds.

Alkylation reactions are widely used in industry. At present, they underlie the synthesis of both the components of high-octane motor fuel and the initial products for making synthetic rubbers and resins, detergents, plastics, lacquers, solvents, benzene homologues, ethers, esters, fatty aromatic ketones, amines, and ammonium and sulphonium compounds.

Alkylation reactions can be divided into several groups. One group of reactions is the introduction of an alkyl into a carbon chain, such as when *sec*-butylbenzene and isooctane are obtained. Another group of reactions consists in the introduction of alkyls instead of hydrogen into the hydroxyl group, leading to the formation of ethers, and the introduction of alkyls into amines with the formation of alkylamines and tertiary fatty aromatic amines. Alkylation reactions include the Friedel-Crafts reaction for aromatic hydrocarbons, which will be considered in Chapter 10.

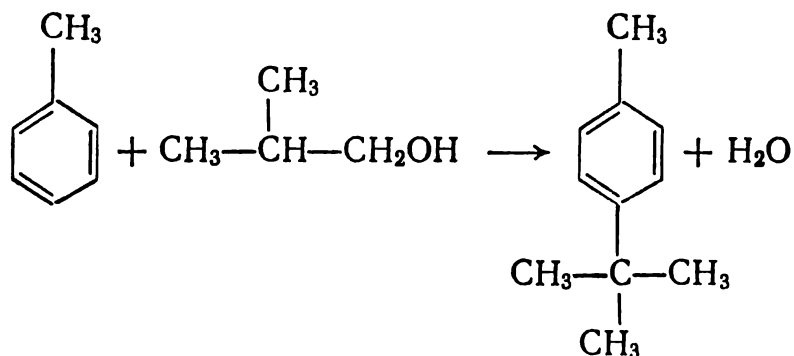
Alkylation can be carried out by various agents, those most widely used being olefins, alcohols, halogen derivatives and dialkyl sulphates.

8.1. ALKYLATION OF AROMATIC HYDROCARBONS BY ALCOHOLS IN THE PRESENCE OF SULPHURIC ACID

Aromatic hydrocarbons can be alkylated by alcohols in the presence of sulphuric acid (as well as AlCl_3 , HF , P_2O_5 and H_3PO_4). In this reaction, good results are obtained when use is made of higher aliphatic alcohols, especially the tertiary ones. The proton of sulphuric acid (H^+) with a molecule of alcohol gives the carbonium ion $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2^+$, which is isomerized into the stable ion $\text{CH}_3\text{—CH}_2\text{—}\overset{+}{\text{C}}\text{H—CH}_3$. The latter is an alkylating agent.

Alkylation depends on the nature of the substituents in the nucleus. The presence of halogens and the nitro and sulpho groups impedes the introduction of the alkyl radical. The presence of the alkyl group in the nucleus promotes further alkylation, and in this

case mainly para-substituents are obtained; for instance, 1-methyl-4-*tert*-butylbenzene is obtained from toluene and isobutyl alcohol:



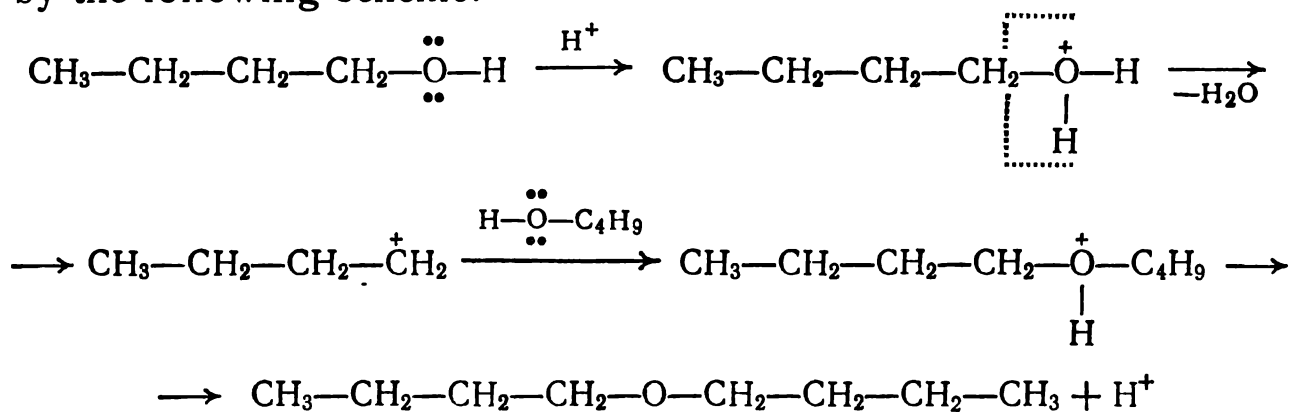
When aromatic hydrocarbons are being alkylated by alcohols in the presence of sulphuric acid, the latter is heated to 70-80 °C and, while stirring, a mixture of aromatic hydrocarbon and alcohol is slowly poured in during the course of 3-5 h.

8.2. PREPARATION OF ETHERS

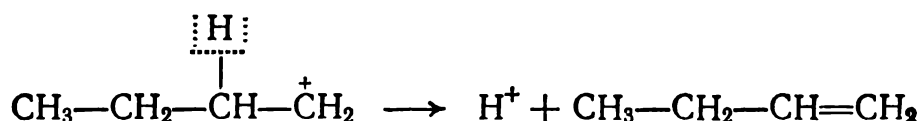
Ethers are obtained by dehydrating alcohols, by allowing alkyl halides to act on alkoxides and phenoxides, and dialkyl sulphates on phenoxides, and by other methods.

Ethers are formed by alcohol dehydration only in the presence of hydrogen ions, which act as catalysts. The acid reagent used depends on the properties of the alcohol which forms ether. Sulphuric acid is employed in most cases, but use is also made of hydrogen chloride, sulphonic and phosphoric acids, etc.

For instance, the formation of dibutyl ether can be represented by the following scheme:



Olefins are formed when ethers are obtained as by-products:



The reactions of polymerization, carbonization and the reduction of sulphuric acid to SO₂ occur simultaneously.

The interaction between alkyl halides and alkoxides or phenoxides is of great importance. It can be used to convert various organic compounds with alcoholic and phenolic hydroxyl groups into ethers, mixed ethers, and fatty aromatic ethers. Of all the alkyl halides, it is best to use iodides (iodides > bromides > chlorides). The reaction is usually carried out in a flask fitted with a reflux condenser. The reaction is over when moist litmus paper no longer shows an alkaline reaction.

Fatty aromatic ethers are obtained from phenoxides (sodium ethoxide + phenol) and alkyl halides; in this case, the reaction occurs as readily as it would in those involving alkoxides. The reaction in which the alkyl group is substituted for the hydrogen of the hydroxyl group of phenol can be easily carried out by allowing dialkyl sulphates (dimethyl- or diethyl-sulphates) to act on phenol in the presence of alkali.

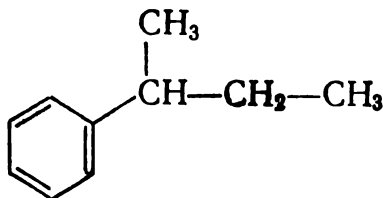
Phenol is usually dissolved in a required amount of an aqueous solution of sodium hydroxide, and dialkyl sulphate slightly exceeding the necessary amount is added while stirring or shaking the solution. In most cases, the reaction product is separated out as a precipitate or an oil. The reaction occurs readily in the cold or at slightly elevated temperatures, but in such instances only one alkyl group of dialkyl sulphate will react.

Since sulphuric acid esters, especially dimethyl sulphate, are very *poisonous*, all operations involving them should be carried out under a hood with great care.

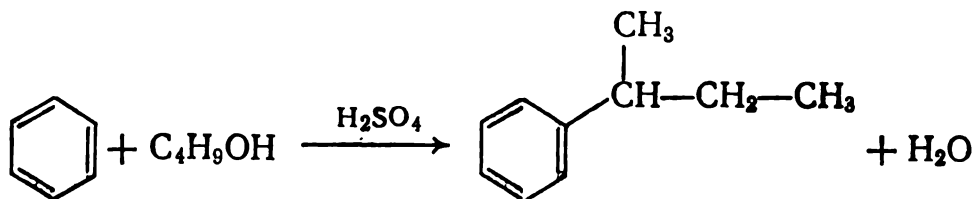
8.3. SYNTHESSES

sec-BUTYLBENZENE

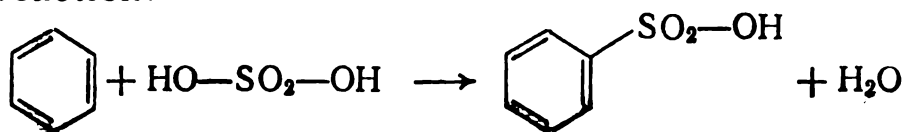
Formula:



Main reaction:



Side reaction:



Reagents and Equipment

Benzene	29 g or 33 ml (0.37 mole)	Flask, three-neck round-bottom (500 ml)	1
Butyl alcohol	11 g or 14 ml (0.15 mole)	Condenser, Liebig	1
Sulphuric acid, 85 per cent .	75 ml	Stirrer	1
		Funnel, dropping	1
		Funnel, separatory	1
		Apparatus, fractional distillation	1
		Receivers	2

Assembly

1. A 500-ml three-neck, round-bottom flask, placed in a water bath, is fitted with a reflux condenser, a dropping funnel and a stirrer.

2. Fractional distillation apparatus (see Fig. 1.11).

Procedure

Seventy-five millilitres of a 85 per cent sulphuric acid are poured into a 500-ml three-neck, round-bottom flask and a mixture consisting of 33 ml of benzene and 14 ml of butyl alcohol is added dropwise from the dropping funnel for one hour while vigorously stirring the solution and heating it in a water bath at 70-80 °C.

1. The concentration of the acid must be strictly maintained at a definite level since this greatly affects the yield.

2. The experiment is carried out while vigorously stirring the solution so that the reaction mixture does not separate into two immiscible layers of sulphuric acid and benzene.

3. The temperature conditions must be watched closely because the reaction occurs very slowly at 55 °C, while the products begin to sulphonate when the temperature rises to 95 °C.

After the mixture is introduced, stirring is continued for another five hours at the same temperature.

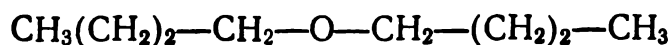
Care should be taken when working with benzene because after some time benzene vapours cause headaches, weariness and drowsiness.

After the reaction, the contents of the reaction flask are poured into a separatory funnel, the upper hydrocarbon layer is separated and washed twice with water, dried over calcium chloride and then transferred to a round-bottom flask and subjected to fractional distillation. Two fractions, one up to 172 °C and the other 172-172.5 °C, are collected. The last fraction is pure *sec*-butylbenzene. The yield of *sec*-butylbenzene is 9 g.

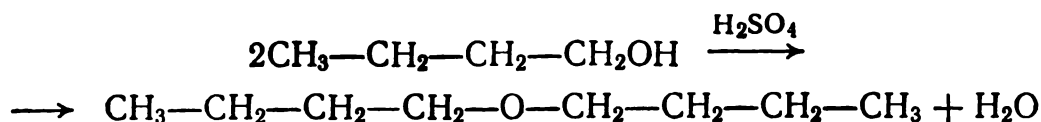
sec-Butylbenzene is a liquid whose b.p. is 170-174 °C; d_4^{20} , 0.8606-0.8639; and n_D^{20} , 1.4885-1.4902.

DIBUTYL ETHER

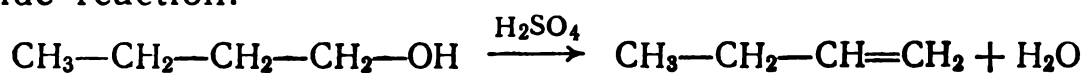
Formula:



Main reaction (for the reaction mechanism, see p. 151):



Side reaction:

*Reagents and Equipment*

Butyl alcohol	50 g or 62 ml (0.67 mole)	Flasks, round-bottom (100 and 200 ml)	2
Sulphuric acid ($d = 1.84$) .	7 ml (0.13 mole)	Head, still	1
Sodium hydroxide, 3 <i>N</i> solution	200 ml	Dephlegmator	1
Calcium chloride		Thermometer	1
Sodium, metallic		Condenser, Liebig	1
		Funnel, dropping	1
		Funnel, separatory	1
		Adapter, bent	1
		Receivers	2
		Cylinder, graduated	1

Assembly

1. A 200-ml round-bottom flask containing boiling stones is connected to a still head. A dropping funnel is inserted in an arm of the latter. A dephlegmator (with a thermometer), connected to a downflow condenser by a bent adapter whose end is lowered into the receiver, is inserted in the other arm.

2. Device 3 on page 136.

Procedure

Sixty-two millilitres of butyl alcohol are poured into a round-bottom flask of apparatus 1 and 7 ml of concentrated sulphuric acid are added while stirring. The mixture of alcohol and acid is carefully heated over an asbestos gauze while making sure that the temperature of the outgoing vapours does not rise above 100–101 °C (failure to maintain the necessary temperature conditions can lead to the formation of butylene and the products of its polymerization, carbonization, and the reduction of sulphuric acid to SO₂). The distillate is slowly driven off. From time to time, it is separated from the water and transferred to a dropping funnel, from which it is re-introduced dropwise into the reaction flask. Water is poured into a graduated cylinder. In three or four hours, when 10 ml of water have been driven off, the distillate is separated

from the water, re-introduced into the flask and boiled for another 15-20 min. Then heating is stopped.

The contents of the flask are cooled, 30 ml of 3 *N* sodium hydroxide solution are added while stirring and cooling the solution, and the mixture is then transferred to a separatory funnel. The mixture is washed with an alkaline solution until the wash waters show an alkaline reaction. The ethereal layer is then washed with 30 ml of water and the same amount of a saturated calcium chloride solution. The layer is carefully separated into a dry bottle and dried by calcium chloride.

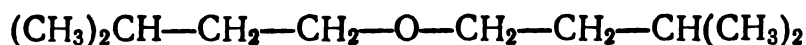
The dried ethereal layer is filtered off and distilled from a 110-ml round-bottom flask with a dephlegmator. The distillate up to 135 °C is collected. The residue in the flask is then cooled, a piece of metallic sodium is put into it (*wear safety glasses!*) and dibutyl ether is distilled, collecting it at 140-145 °C (do not distill to dryness — there can be an *explosion!*). The yield of dibutyl ether is about 25 g.

Dibutyl ether is a colourless liquid. Its molecular weight is 130.22; b.p., 141.97 °C; m. p., — 95.37 °C; d_4^{20} , 0.7688, and n_D^{20} , 1.3992.

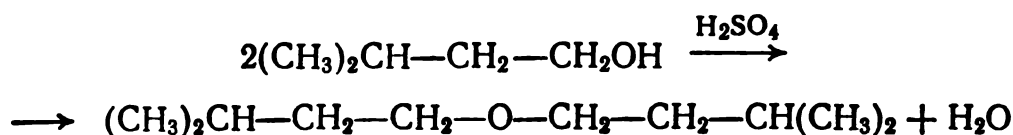
It is employed as a solvent and is used in Grignard's synthesis. Explosive peroxides are formed when dibutyl ether is stored for a long time. A test for their content is therefore carried out before it is used.

ISOAMYL ETHER

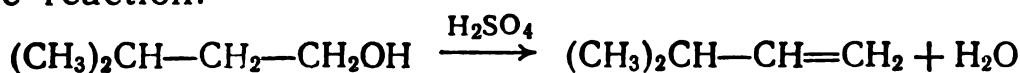
Formula:



Main reaction (for the reaction mechanism see p. 151):



Side reaction:



Reagents and Equipment

Isoamyl alcohol	50 g or 62 ml (0.57 mole)	Flask, round-bottom (200 ml) . . .	1
Sulphuric acid ($d = 1.84$)	2 ml (0.04 mole)	Attachment for separating water . .	1
Potassium carbonate		Condenser, Liebig	1
		Apparatus, steam distillation . . .	1
		Funnel, separatory	1
		Flask, Würtz (100 ml)	1
		Condenser, air	1
		Thermometer	1
		Receivers	2

Assembly

1. A 200-ml round-bottom flask is connected by cork stoppers to an attachment for separating water, and also to a reflux condenser (Fig. 8.1).

2. Steam distillation apparatus (see Fig. 3.6).

3. A 100-ml Würtz distilling flask fitted with a thermometer is connected to a downflow air condenser, the end of which is lowered into the receiver.

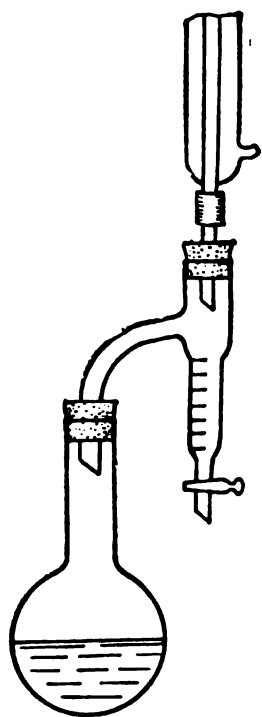


Fig. 8.1. Apparatus with an attachment for separating water

Procedure

Sixty-two millilitres of freshly prepared isoamyl alcohol and 2 ml of concentrated sulphuric acid are poured into a 200-ml round-bottom flask. The mixture formed is slightly boiled for several hours until 4 ml of water collect in the water separator. The contents of the flask are cooled to 100 °C and distilled with steam. Distillation is carried on until oily drops no longer pass to the distillate. The distillate is then transferred to a separatory funnel and ether is separated from the water layer into a dry flask and dried by a small amount of calcined potassium carbonate.

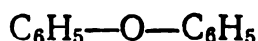
The dried ether is put in a 100-ml Würtz flask, which is connected to the air condenser. The flask is then slowly heated. Some amylene is driven off at 21 °C; unreacted isoamyl alcohol begins to be driven off at 128 °C, and isoamyl ether is driven off at 165-172 °C.

The isoamyl ether obtained contains impurities. To obtain a pure product, it is boiled with one gram of sodium amide, driven off, shaken with dilute sulphuric acid in a separatory funnel, dried by calcium chloride and distilled over metallic sodium. The yield of isoamyl ether is about 25 g.

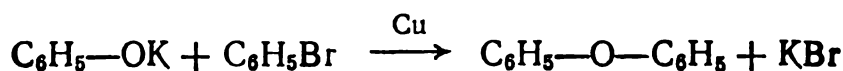
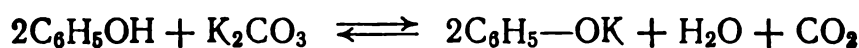
Isoamyl ether is a liquid whose b.p. is 172 °C and d_{15}^{15} , 0.7807.

DIPHENYL ETHER

Formula:



Main reactions:



Reagents and Equipment

Phenol 17 g	Flask, round-bottom (250 ml) 1
(0.18 mole)	Condenser, air 1
Bromobenzene . . 15.7 g or 10.5 ml	Apparatus, steam distillation 1
(0.1 mole)	Flask, Bunsen 1
Potassium carbonate 15 g	Funnel, Büchner 1
Copper, powdered . 0.2 g	Flask, safety 1
Sodium hydroxide, 10 per cent solution	Thermometer 1
	Receivers 2

Assembly

1. A 250-ml round-bottom flask fitted with a long reflux air condenser is placed in an oil bath in which a thermometer is immersed.
2. Steam distillation apparatus (see Fig. 3.6).
3. Suction apparatus (see Fig. 2.21).

Procedure

Work should be done *in a fume cupboard!* Put 17 g of phenol (**caution:** phenol is poisonous and causes severe skin burns; gloves should be worn when working with it) in a 250-ml round-bottom flask and heat it on an asbestos gauze to 42-45 °C. When the phenol melts, heating is stopped and 15 g of calcined and finely ground calcium carbonate (KOH can be used; reactions with NaOH are slow), 10.5 ml of dry, freshly distilled bromobenzene and 0.2 g of copper powder are added. The mixture is heated in an oil bath for two hours at 210 °C. The flask is then cooled and, in order to wash phenol away from the crude diphenyl ether, a 10 per cent sodium hydroxide solution is added to the reaction mixture until the solution reacts alkaline.

Apparatus 2 is assembled and the steam distillation of the mixture is commenced. At first, unreacted bromobenzene is driven off. As soon as diphenyl ether crystals begin to appear in the condenser, the receiver is changed and the fraction collected. The diphenyl ether obtained is sucked off in the Büchner funnel and dried on filter paper. The yield of diphenyl ether is about 14 g.

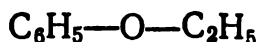
Diphenyl ether which is contaminated by phenol turns yellow in the light and crystallizes poorly. To purify diphenyl ether, it can be recrystallized out of a 50 per cent ethyl alcohol solution.

Diphenyl ether (phenoxybenzene, diphenyl oxide) consists of colourless crystals with a geranium-like odour; it does not dissolve in water, but dissolves well in ether and benzene. Its molecular weight is 170.2; b.p., 259.3 °C; m.p., 26-27 °C; d_4^{30} , 1.066, and n_D^{30} , 1.5762.

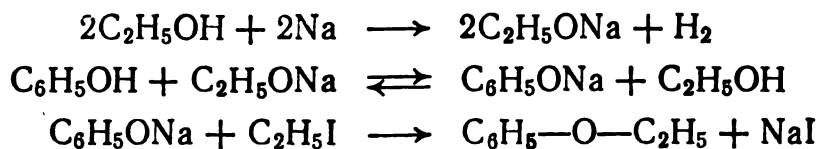
It is used as a heat carrier and for scenting soap.

PHENETOLE

Formula:



Main reactions:

**Reagents and Equipment**

Phenol	9.4 g (0.1 mole)	Flask, round-bottom (100 ml) .	1
Sodium, metallic . . .	2.3 g (0.1 gram atom)	Flask, Würtz (100 ml)	1
Ethyl iodide	20 g or 15.4 ml (0.13 mole)	Condenser, Liebig	1
Ethyl alcohol, absolute	30 ml	Funnel, separatory	1
Sodium hydroxide, 10 per cent solution		Flask, conical	1
Calcium chloride		Condenser, air	1
Ethyl ether		Adapter, bent	1
		Thermometer	1
		Receivers	2

Assembly

1. A 100-ml round-bottom flask is connected to a reflux condenser and placed in a water bath.

2. A 100-ml round-bottom flask is connected by a stopper with a bent glass tube to a Liebig condenser, which has a bent adapter that is lowered into a receiver.

3. Apparatus 3 on page 156.

Procedure

Thirty millilitres of absolute ethyl alcohol are poured into the round-bottom flask of apparatus 1 (since ethyl ether dissolves sodium phenoxide and ethyl iodide well, the reaction is carried out in an alcoholic solution, thus ensuring the homogeneity of the medium and the ready occurrence of the reaction) and 2.3 g of metallic sodium are gradually added. Then, 9.4 g of phenol, which have been dissolved in absolute alcohol, and 20 g of ethyl iodide are put in the flask. The mixture is heated in a water bath fitted with an air condenser not until it boils, because ethyl iodide is volatile, but until the litmus test shows that the alcoholic solution no longer produces an alkaline reaction. Afterwards, apparatus 2 is assembled and ethyl alcohol is driven off, while water is added to the residue in order to dissolve sodium iodide which has separated out in the reaction. The contents of the flask are transferred to a separatory funnel and phenetole is extracted by diethyl ether.

The upper layer of the ethereal solution is separated. To remove unreacted phenol, the ethereal layer is shaken with a sodium hydroxide solution in a separatory funnel. The ethereal extract is then separated again, transferred to a conical flask and dried by calcium chloride. Ether is distilled from the flask fitted with an air condenser at 34-36 °C and then phenetole is driven off at 167-172 °C (apparatus 3). The yield of phenetole is about 9 g.

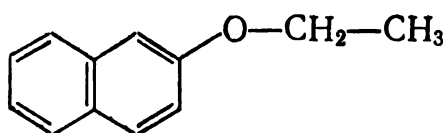
Phenetole (phenyl ethyl ether) is a colourless liquid with an aromatic odour, insoluble in water, but miscible with alcohol and ether. Its molecular weight is 122.16; b.p., 172 °C at 760 mm Hg; m.p., -29.5 °C; d_4^{20} , 0.9651; and n_D^{20} , 1.5076.

It is used, together with ethylene glycol, in saponifying ethers that are cleaved with difficulty by potassium hydroxide. It is also employed as a solvent for crystallizing organic compounds. Phenetole acts narcotically on the organism.

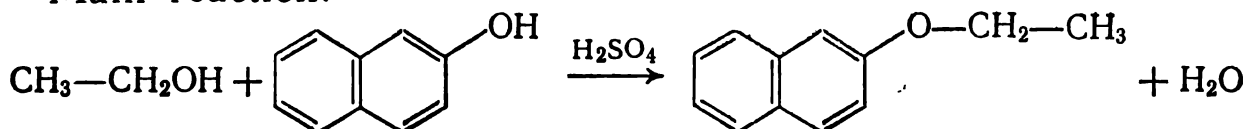
Characterization Test. When phenetole with 48 per cent hydrobromic acid is heated until the mixture boils, phenetole decomposes into phenol and volatilizing ethyl bromide.

β-NAPHTHYL ETHYL ETHER (NEW NEROLIN, BROMELIA)

Formula:



Main reaction:



Reagents and Equipment

β-Naphthol	25 g (0.17 mole)	Flask, round-bottom (100 ml) . . .	1
Ethyl alcohol, absolute . . .	38 ml (0.6 mole)	Flask, conical, wide-mouth (250 ml)	1
Sulphuric acid ($d = 1.84$) . .	5.5 ml (0.09 mole)	Condenser, Liebig	1
Sodium hydroxide, 5 per cent solution	90 ml	Stirrer	1
		Funnel, Büchner	1
		Flask, Bunsen	1
		Flask, safety	1

Assembly

1. A 100-ml round-bottom flask is connected to a reflux condenser and placed in a glycerol or air bath.
2. Suction apparatus (see Fig. 2.21).

Procedure

Twenty five grams of β -naphthol are put in a 100-ml round-bottom flask and 38 ml of absolute ethyl alcohol are added (see p. 42). The flask is carefully shaken until the greater part of β -naphthol dissolves and then 5.5 ml of concentrated sulphuric acid are added (intense heating of the mixture is observed). The flask is put in a water bath and heated to boiling for 3-4 h. After heating, the warm solution is poured into a 250-ml conical flask which contains 90 ml of a 5 per cent sodium hydroxide solution heated to 50°C. In this case, nerolin settles as dark oil, which is mixed with the alkaline solution by a stirrer until it solidifies completely. To preclude the instantaneous solidification of crude nerolin the alkaline solution should be heated well while the reaction mixture is being poured into it. The conical flask should therefore be carefully heated in a water bath.

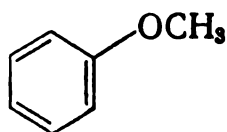
The sandy coloured precipitate is filtered off in the Büchner funnel and treated again with the previous amount of a sodium hydroxide solution. Nerolin is sucked off, washed with water until the litmus test no longer shows an alkaline reaction, and dried at a temperature not higher than 50°C.

The dried product is distilled with steam superheated to 150°C. When need be, the product may be purified by recrystallization from alcohol or by vacuum distillation (b.p. 140°C at 12 mm Hg). The yield of β -naphthyl ethyl ether is about 24 g.

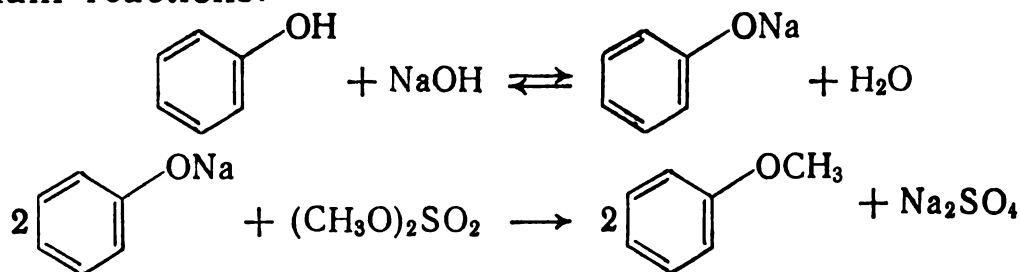
β -Naphthyl ethyl ether consists of white crystals which boil at 282°C and melt at 37.5°C. It dissolves in most organic solvents, and is used for scenting soap.

ANISOLE

Formula:



Main reactions:



Assembly

1. Apparatus 1 on page 159 (a 150-ml round-bottom flask is employed in the apparatus used here).
2. Apparatus 3 on page 136.

Reagents and Equipment

Phenol	12 g (0.12 mole)	Flasks, round-bottom (150 and 100 ml)	2
Dimethyl sulphate . .	8 g or 5.8 ml (0.05 mole)	Condenser, Liebig	1
Benzene	13 ml	Funnel, separatory	1
Sodium hydroxide . .	5.5 g	Dephlegmator	1
Calcium chloride . . .	1.5 g	Thermometer	1
		Adapter, bent	1
		Receivers	2

Procedure

A solution of 5.5 g of sodium hydroxide in 40 ml of water is prepared in a round-bottom flask of apparatus 1 and 12 g of phenol are dissolved in it. After cooling the contents of the flask to 15°C, 2 ml of dimethyl sulphate are added to the solution obtained. (Dimethyl sulphate is a poison! Work should be done *in a fume cupboard*.) After being closed with a cork stopper which is fitted with a thermometer and has a side slit, the flask is shaken for 20 min, cooling it from time to time (the temperature of the mixture should not be higher than 40°C).

After shaking the flask for 20 min, another 2 ml of dimethyl sulphate are added, and it is shaken again for another 30 min. The remaining dimethyl sulphate is then added and the reaction mixture is heated in a boiling water bath for one hour in a flask which is fitted with a reflux air condenser so as to complete the reaction and to hydrolyze unreacted dimethyl sulphate. Afterwards, anisole is separated in a separatory funnel and the partially remaining anisole is extracted from the lower aqueous layer by benzene (see p. 62).

The benzene extract is combined with the anisole separated earlier and is dried by calcium chloride. Benzene is then driven off in a boiling water or sand bath (apparatus 2) at 80-85°C and anisole is distilled, collecting it at 154-156°C. The yield of anisole is about 7.5 g.

Anisole (methoxybenzene, phenylmethyl ether) is a colourless liquid with an aromatic odour; it does not dissolve in water, but readily dissolves in alcohol, ether and benzene, and is easily distilled with steam. Its molecular weight is 108.13; b.p., 155°C; m.p., -37.4°C; d_4^{20} , 0.9940; and n_D^{20} , 1.5170.

It is employed as a solvent in perfumery and is used for crystallization.

Characterization Tests. 1. Anisole produces a dark green colour when it is heated with a 5 per cent solution of selenious acid in concentrated sulphuric acid.

2. It produces a cherry red colour with vanillin and hydrochloric acid.

Chapter 9

ACYLATION REACTIONS

The acylation reaction is the replacement of the hydrogen atom of certain functional groups, i.e., the hydroxyl, amino and other groups, by the residue of carboxylic acid: acyl $R-\overset{\overset{O}{\parallel}}{C}-$. Esters

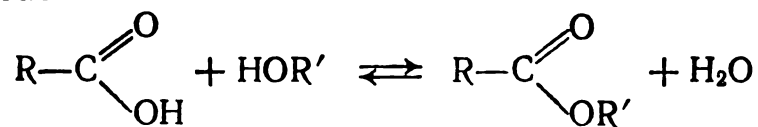
are obtained as a result of alcohol acylation, and mono- and disubstituted amides are obtained in amine acylation.

Besides alcohols and amines, other compounds with mobile hydrogen atoms, e.g., mercaptans and phenols, are also readily acylated. The production of aromatic ketones by the interaction of aromatic hydrocarbons with acid chlorides or anhydrides in the presence of aluminium chloride (the Friedel-Crafts reaction) can be included in the acylation reactions of a special type.

The acylating agents used are carboxylic acids or, more frequently, ethers of greater reactivity, or acid chlorides or anhydrides. Mixed anhydrides of silicic and carboxylic acids, e.g., $(CH_3COO)_4Si$, are also effective acylating agents.

9.1. ACYLATION OF ALCOHOLS AND AMINES BY CARBOXYLIC ACIDS

Esters and water are formed when alcohols are acylated by carboxylic acids:



This reaction is known as direct esterification. The kinetics of esterification have been considered in detail by N. A. Menshutkin and his pupils in several works (1877-1891). Esterification is an example of a reversible reaction.

It has been shown experimentally that if equimolecular amounts of initial substances are introduced into a reaction, the rate of the forward reaction will be high, and that of the reverse reaction will be negligible at the beginning of the reaction in conformity with the law of mass action. As ester and water are formed, the rate of the reverse reaction rapidly increases until there is dynamic equilibrium, in which the amount of the ester and water being formed is equal to that of alcohol and acid that is obtained in ester hydro-

lysis per unit time. Therefore, only about two-thirds of acid and alcohol react, forming ester and water.

To shift equilibrium towards product formation, i.e., to increase the ester yield, it is necessary to take an excess of acid or alcohol for the reaction or remove the ester or water being formed from the reaction sphere. Ester is driven out of the reaction flask when low-boiling esters (e.g., ethyl acetate, b.p. 77 °C) are being obtained, and water is driven out when high-boiling esters (iso-amyl acetate, b.p. 142 °C) are being obtained.

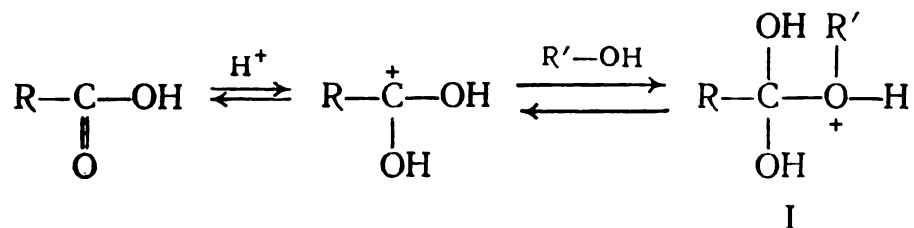
It is better to remove water by azeotropic distillation (azeotropic esterification) in many cases, especially when unstable compounds are involved, because smaller amounts of a catalyst can then be employed and an excess of acid or alcohol does not have to be used. The solvent with which water is driven off is selected with regard to the boiling point of the lowest-boiling component of the reaction mixture. Chloroform, carbon tetrachloride, benzene and toluene are usually used for removing water as an azeotropic mixture.

The interaction between acids and alcohols at room temperature occurs slowly because of the low activity of the carbonyl group in acids. Because of the effect of the hydroxyl group, which reduces the positive charge on the carbonyl carbon, the carbonyl group, being bound with the hydroxyl group in acids, is less reactive than it is in aldehydes and ketones. The more rapid the esterification of carboxylic acid, the higher the positive charge of the carbonyl carbon, i.e., the stronger the acid. For instance, formic and oxalic acids (strong acids) rapidly react with alcohols.

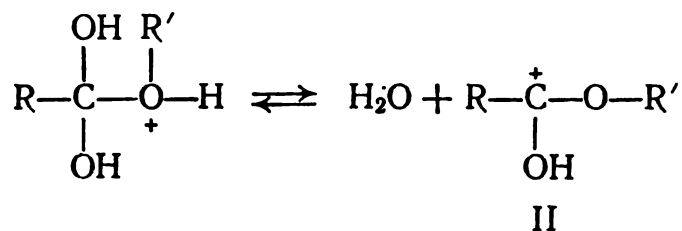
To increase the reaction rate, the temperature is elevated and catalysts are used, such as hydrogen ions (protons), which are obtained in the dissociation of strong mineral acids, mostly concentrated sulphuric acid and dry hydrogen chloride. In the presence of mineral acids, the esterification rate increases as much as the ester hydrolysis rate. Therefore, equilibrium is exactly the same when a catalyst is present as when it is absent. Thus, catalysts increase the reaction rate, but do not shift equilibrium. This is true of all reversible reactions which occur in the presence of catalysts.

Concentrated sulphuric acid is often used in esterification reactions, because, being a strong acid, it is a source of hydrogen ions. Even its small addition acts catalytically, while the introduction of large amounts of it into the reaction medium binds the water being formed. This positively affects the ester yield. But in a strongly acidic medium, there is a greater tendency towards the formation of ethers and olefins from alcohols. In most cases, the amount of sulphuric acid used is 5-10 per cent of the alcohol used in a reaction.

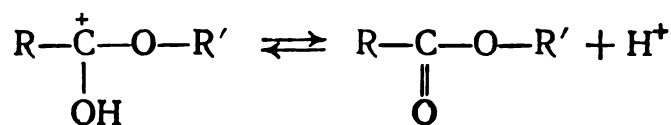
What an acid (catalyst) does is to add a proton to the carbonyl oxygen. This increases the positive charge on the carbon atom of the carboxyl group and makes the addition to it of the nucleophilic reagent, i.e., alcohol, more active:



Complex I is capable of reversibly decomposing with the elimination of water and the formation of an ester carbonium ion:



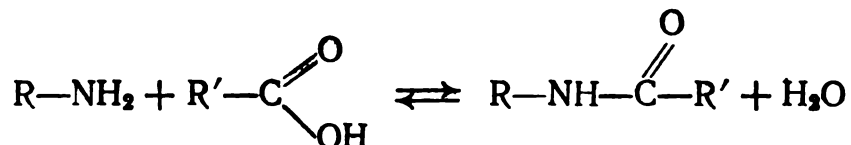
In dissociation, the carbonium ion II forms an ester and a proton (i.e., the catalyst is reactivated):



If sulphuric acid can cause a side reaction, aromatic sulphonic acids or, even better, dry hydrogen chloride which is passed through the reacting alcohol, may be used instead.

The acylation of alcohols by carboxylic acids gives good results only when primary alcohols and low-molecular-weight acids are used. Secondary alcohols give about 40 per cent of the ester yield, and tertiary ones, only 3 per cent. Therefore, esters can be obtained when carboxylic acids act directly on the alcohols only by using primary and secondary alcohols.

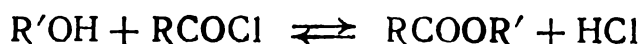
Amines are acylated by carboxylic acids as shown in the following scheme:



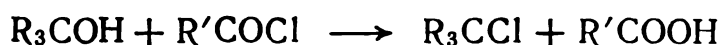
The reaction occurs more rapidly if the acid has a low molecular weight.

9.2. ACYLATION OF ALCOHOLS, PHENOLS AND AMINES BY ACYL CHLORIDES

When alcohols and phenols are acylated by acyl chlorides, esters are obtained by the following scheme:



Only primary and secondary alcohols readily enter into this reaction with the formation of esters; tertiary alcohols often form chlorine-substituted hydrocarbons under the action of acyl chlorides:



As a rule, acyl chlorides react readily with alcohols and phenols. If the reaction occurs too vigorously, it is necessary to cool the mixture or use solvents (benzene, toluene, etc.). The residue of unreacted acyl chloride is removed by treating the mixture with a sodium carbonate solution. The ester obtained is purified by distillation or crystallization.

Good results are often obtained by using pyridine (sometimes quinoline) as a solvent. This method is especially convenient for acylating compounds which contain several hydroxyl groups (poly-atomic alcohols, sugars, phenols, etc.). Alcohol or phenol is usually dissolved in pyridine, the solution is cooled and an acyl chloride is added to it. After several hours of standing at room temperature, the reaction mixture (dark red) is poured into dilute sulphuric acid to which a small amount of ice has been added beforehand. In this case, acyl derivatives are separated as an oil or a solid. The reaction product is extracted by ethyl ether or chloroform and the extract is washed with dilute acid so as to completely eliminate pyridine. If a chloride of a sparingly soluble acid is used, its excess is removed by washing the extract with a dilute sodium carbonate solution. When pyridine is used, however, by-products are often formed, which can contaminate the main product of a reaction.

Acylation with water-resistant acyl chlorides is carried out in dilute NaOH or KOH solutions. Acyl chloride is usually added gradually to a solution or suspension of either alcohol or phenol in 10 per cent of alkali. If the mixture becomes heated, it is cooled by water with ice.

An excess of acyl chloride is taken. In an alkaline medium, it slowly turns into a water-soluble sodium salt of the appropriate acid. Ester separates as an oil or a precipitate in the course of the reaction.

The acylation of alcohols and phenols by acyl chlorides is widely used in preparative organic chemistry, especially for identifying alcohols and phenols.

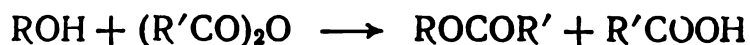
When amines are acylated by acyl chlorides, an acyl derivative and amine chloride are formed:



Amine chloride is separated from its acyl derivative on the basis of their different solubilities. The reaction is usually carried out in a solvent in which the amine salt is insoluble. Moreover, if the acyl derivative of amine is water-insoluble, the chloride can be easily removed by washing the reaction mixture with water. This method of acylating amines by acyl chlorides is usually used for obtaining the benzoyl and aryl sulphonyl derivatives of aromatic amines.

9.3. ACYLATION OF ALCOHOLS, PHENOLS AND AMINES BY ACYL ANHYDRIDES

Acyl anhydrides react with alcohols and phenols, forming esters by this scheme:



This interaction occurs more slowly than the acylation of alcohols and phenols by acyl chlorides.

Acylation is carried out by treating alcohol or phenol with anhydride, either directly or in a solvent medium (e.g., when aspirin is obtained). The reaction can be accelerated by adding a small amount of concentrated sulphuric acid, zinc chloride, sodium acetate or pyridine. The duration of the reaction and the temperature depend on the nature of the compound being acylated.

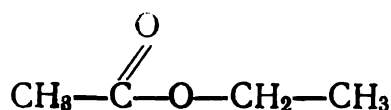
Cyclic anhydrides of dibasic acids act similarly in this reaction.

Amines are very rapidly acylated by acyl anhydrides with high yields. This reaction can be carried out by heating amine with acetic anhydride for several minutes. The reaction product is poured into water and the crystalline acyl derivative is sucked off. The reaction can be carried out in a benzene medium as well. In this case, amine is dissolved in benzene and anhydride is gradually added. The reaction is exothermic, and therefore the solvent boils (*caution: there may be an ejection*). If the acyl derivative is sparingly soluble in benzene, it precipitates on cooling.

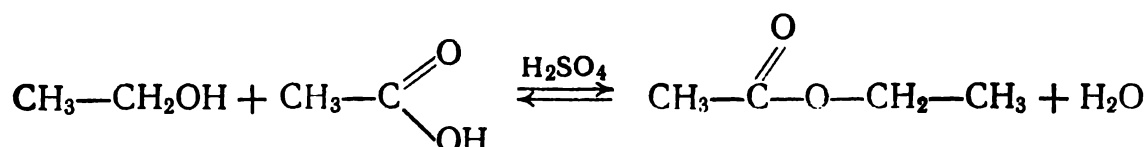
9.4. SYNTHESSES

ETHYL ACETATE

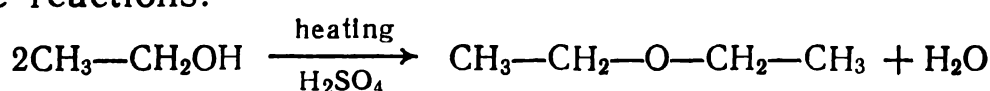
Formula:



Main reaction (for the reaction mechanism, see p. 164):



Side reactions:



This method of obtaining ethyl acetate is based on the binding of water by a dehydrating agent (sulphuric acid); however, azeotropic water distillation can be employed, using chloroform or carbon tetrachloride as a solvent.

Ethyl acetate is *highly flammable* and forms *explosive mixtures* with air.

Reagents and Equipment

Ethyl alcohol, 95 per cent . . .	22.5 ml (0.37 mole)	Flask, Würtz (100 ml)	1
Acetic acid, glacial	20 ml (0.3 mole)	Funnel, dropping	1
Sulphuric acid ($d = 1.84$) . . .	2.5 ml	Condenser, Liebig	1
Calcium chloride	8 g	Thermometer	1
Sodium carbonate, 2 per cent solution		Adapter, bent	1
Sodium sulphate, anhydrous		Funnel, separatory	1
		Receivers	2

Assembly

1. A dropping funnel is inserted into the neck of a 100-ml Würtz distilling flask. The side arm of the flask is connected to a Liebig condenser fitted with a bent adapter which is lowered into a receiver. The flask and a thermometer are placed in an oil bath.

2. A thermometer is inserted into a 100-ml Würtz flask placed in a water bath and the flask is connected to a downflow condenser fitted with a bent adapter whose end is lowered into a receiver.

Procedure

Put 2.5 ml of ethyl alcohol and the same amount of concentrated sulphuric acid in a 100-ml Würtz distilling flask and heat the mixture in an oil bath to 140°C. It can be heated in a sand bath, but then a thermometer must be put in the flask, immersing

its bulb in the liquid, and the mixture should be heated to 110-120 °C.

When 140 °C is reached, a mixture of 20 ml of ethyl alcohol and the same amount of glacial acetic acid (see p. 138) is gradually added from a dropping funnel at such a rate that the ethyl acetate being formed is driven off. In this case, the preset temperature of 140 °C must be constantly maintained because ethyl ether is formed at a higher temperature.

A certain amount of ethyl alcohol is driven off together with the ethyl acetate, and therefore excess alcohol is used and the yield estimated on the basis of the amount of acetic acid used.

After the reaction, which lasts about two hours, the distillate, which, besides ethyl acetate, contains unreacted acetic acid and alcohol, is shaken with a 2 per cent sodium carbonate solution in a separatory funnel (so as to remove acetic acid) until the litmus test shows that the upper layer is neutral or weakly alkaline. (The sodium carbonate solution should be added gradually, since the liquid greatly froths due to the liberation of carbon dioxide.) The lower water layer is then separated, and the upper ethereal layer is shaken with a saturated calcium chloride solution (8 g of calcium chloride in 8 ml of water) in order to remove ethyl alcohol impurities. The upper ethereal layer is separated again and dried by anhydrous sodium sulphate. After drying, the product is distilled in a water bath (apparatus 2).

Calcium chloride with primary alcohols gives the crystalline compound $\text{CaCl}_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$, which does not dissolve in ethyl acetate.

The mixture of alcohol and ethyl acetate is driven off at 71-75 °C, and comparatively pure ethyl acetate, at 75-78 °C.

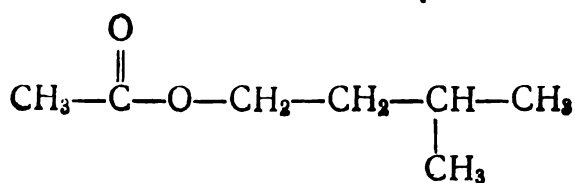
The yield of ethyl acetate is about 20 g. Its practical yield is usually not more than 70 per cent of its theoretical yield, because some ester is lost owing to its volatility and high solubility.

Ethyl acetate (acetic ester) is a colourless liquid with a fruity odour; it dissolves in water and mixes with alcohol, chloroform, benzene and other organic solvents. Its molecular weight is 88.10; b.p., 77.2 °C; m.p., -83.6 °C; d_4^{20} , 0.9006; and n_D^{20} , 1.3724.

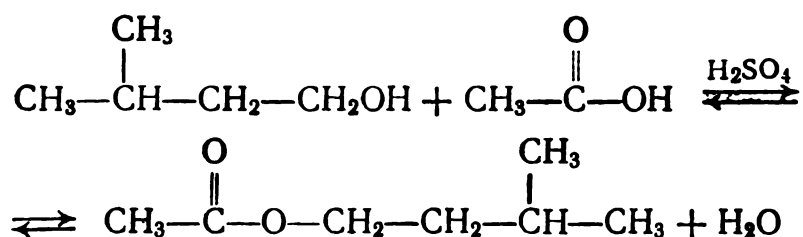
It is used as a solvent of nitrocellulose, Celluloid, fats, wax and resins. It is also employed in analytical chemistry and is used for obtaining ethyl acetoacetate and acetylacetone. It acts narcotically on the organism and irritates the mucous membranes.

ISOAMYL ACETATE

Formula:



Main reaction:



Care should be taken when using isoamyl acetate, because it is *highly flammable* (its flash point is 36 °C).

Preparation of Isoamyl Acetate by Water Removal by Azeotropic Benzene Distillation

Reagents and Equipment

Isoamyl alcohol	22 g or 26 ml (0.25 mole)	Flasks, round-bottom (100 ml)	2
Acetic acid, 80 per cent .	20 ml (0.28 mole)	Attachment ("trap") for separating water	1
Benzene	25 ml	Condenser, Liebig	1
Sulphuric acid ($d = 1.84$)	0.5 ml	Funnel, separatory	1
Acid sodium carbonate, saturated solution		Flask, Würtz (100 ml)	1
		Thermometer	1
		Receivers	4

Assembly

1. A 100-ml round-bottom flask is connected through a separator attachment ("trap") for separating water to a reflux condenser (see Fig. 8.1). The flask is placed in a sand bath.

2. A 100-ml Würtz flask placed in a sand bath is fitted with a thermometer and a Liebig condenser having a bent adapter whose end is lowered into a receiver.

Procedure

Twenty-six millilitres of isoamyl alcohol, 20 ml of acetic acid, 25 ml of benzene and 0.5 ml of concentrated sulphuric acid are poured into a round-bottom flask (apparatus 1; benzene is used as a solvent with which water is driven off as an azeotropic mixture).

The flask is heated in a sand bath (apparatus 1) until the mixture boils intensely. The condensate, which consists of ether, unreacted acid, benzene and water isolated during the reaction, passes from the reflux condenser to the attachment, where it separates into the benzene (upper) and aqueous (lower) layers. The aqueous layer is poured from time to time into a graduated cylinder and measured (about 8-9 ml of water is isolated during the reaction), while the benzene solution flows back into the reaction flask as it accumulates in the attachment (the reaction is considered to be

complete when the water layer in the attachment ceases to change volumetrically).

After the reaction, which lasts three or four hours, the benzene solution which has collected in the attachment is poured back into the flask, apparatus 2 is assembled and benzene is distilled from the reaction mixture at 80-81 °C. The residue is transferred from the flask to a separatory funnel and washed with 50-60 ml of water, and the lower water layer is separated. The ethereal layer which remains in the separatory funnel is shaken successively with 50 ml of water, 20-25 ml of a dilute acid sodium carbonate solution until the solution reacts neutral and again with 25 ml of water. After separating ester from water, it is dried by anhydrous sodium sulphate or calcium chloride. If the water layer is not well separated from the ethereal layer, five grams of common salt should be added and the mixture thoroughly stirred. This salting-out process reduces the water-solubility of ester. Two fractions are then driven off in apparatus 2: (1) up to 110 °C, consisting mainly of the benzene residue, and (2) 136-142 °C. If the temperature range of the second fraction is wider, the fraction is redistilled and isoamyl acetate is collected at 138-142 °C. The yield of isoamyl acetate is 25-27 g.

The foregoing method can be used to obtain butyl acetate, whose boiling point is 124-125 °C.

Preparation of Isoamyl Acetate by Distilling Water Without Benzene

Reagents and Equipment

Isoamyl alcohol	22 g or 26 ml (0.25 mole)	Flasks, round-bottom (100 ml) .	2
Acetic acid, glacial	18 g or 17 ml (0.3 mole)	Attachment ("trap") for separating water	1
Sulphuric acid ($d = 1.84$) .	0.5 ml	Condenser, Liebig	1
Acid sodium carbonate, saturated solution		Funnel, separatory	1
		Dephlegmator	1
		Receivers	2

Assembly

1. Apparatus 1 on page 169.
2. Apparatus 2 on page 169.

Procedure

Twenty-six millilitres of isoamyl alcohol, 17 ml of glacial acetic acid and 0.5 ml of sulphuric acid are poured into a round-bottom flask of apparatus 1. The flask is heated in a sand bath until two layers are formed in the "trap": the lower (water) layer and the upper (ester, unreacted acetic acid and alcohol) layer, which flows back into the reaction flask. The end of the reaction is determined

by the amount of water which is separated (4.5 ml). Otherwise, the reaction is carried on until the water layer no longer increases in the "trap", ester is separated from the water in the separatory funnel and dried by anhydrous sodium sulphate or calcium chloride, and the operation continued as indicated on page 169. The yield of isoamyl acetate is about 27 g.

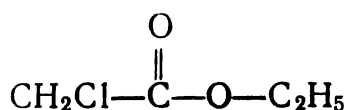
Isoamyl acetate (isoamylacetic ester) is a colourless liquid with a fruity odour; 0.25 g of it dissolves in 100 g of water, and it mixes with alcohol, ether and chloroform. Its molecular weight is 130.18; b.p., 142°C; m.p., -78.5°C; d_4^{20} , 0.8719; and n_D^{20} , 1.4053.

It is employed as a solvent for nitrocellulose and is used in the food industry as a "pear essence". It is also employed as a solvent in analytical chemistry. It acts narcotically on the organism and irritates the mucous membranes of the eyes, nose and respiratory tracts.

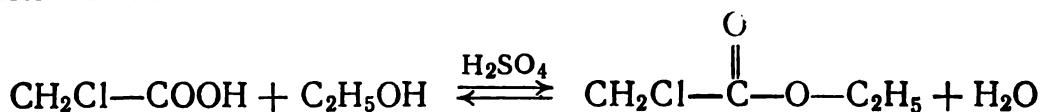
Characterization Test. Two or three millilitres of isoamyl acetate and 3 ml of a 1 per cent solution of ferric chloride in 10 N hydrochloric acid are poured into a test tube. The mixture separates into layers when the test tube is shaken well. The upper ethereal layer is bright brownish-yellow owing to the transition of almost all the iron salt to it. The lower layer is pale yellow.

ETHYL CHLOROACETATE

Formula:



Main reaction:



Care should be taken when working with ethyl chloroacetate, because it *irritates the mucous membranes!*

Reagents and Equipment

Chloroacetic acid	20 g (0.2 mole)	Flask, round-bottom (100 ml) . . .	1
Ethyl alcohol, absolute . . .	12 g or 15 ml (0.26 mole)	Condenser, Liebig	1
Sulphuric acid ($d = 1.84$) . .	1 ml	Tube, calcium chloride	1
Acid sodium carbonate,		Funnel, separatory	1
saturated solution	5 ml	Apparatus, fractional distilla-	
Calcium chloride	2 g	tion	1
		Beaker	1
		Receivers	2

Assembly

1. A 100-ml round-bottom flask is connected to a reflux water condenser to which a calcium chloride tube is attached. The tube is needed for protecting the reaction medium from moisture.

2. Fractional distillation apparatus (see Fig. 1.11).

Procedure

Twenty grams of chloroacetic acid (**caution: chloroacetic acid causes skin burns!**), 15 ml of absolute ethyl alcohol (see Chap. 2) and 1 ml of concentrated sulphuric acid are put in a 100-ml round-bottom flask and the mixture is heated in a sand bath for five hours.

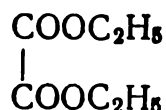
After the reaction, the mixture is cooled and poured into a beaker containing 100 ml of icy water. The mixture is transferred from the beaker to a separatory funnel and the lower water layer is separated. The ethereal layer is neutralized by 5 ml of a saturated acid sodium carbonate solution and washed with water until the solution reacts neutral. Afterwards, crude ethyl chloroacetate is dried for 10-12 h over anhydrous calcium chloride, apparatus 2 is assembled and the fraction which boils at 142-143 °C is driven off. The yield of ethyl chloroacetate is about 19 g.

Ethyl chloroacetate can also be obtained by azeotropic esterification.

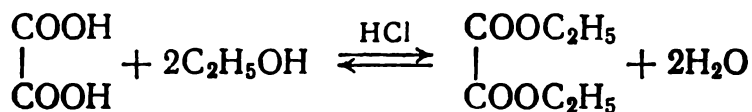
Ethyl chloroacetate is a colourless mobile liquid with a pungent fruity odour. Its b.p. is 144 °C, and n_D^{20} , 1.4227. It is used for obtaining the ester of phenylmethyl glycidic acid.

DIETHYL OXALATE (ETHYL OXALATE)

Formula:



Main reaction:



Reagents and Equipment

Oxalic acid, anhydrous	30 g	Flask, round-bottom, short-necked	
	(0.4 mole)	(150 ml)	1
Ethyl alcohol, absolute	45 ml	Head, still	1
	(0.75 mole)	Condenser, Liebig	1
Sodium carbonate, crystalline	100 g	Tube, calcium chloride	1
Hydrogen chloride gas		Tube, gas	1
Calcium chloride		Apparatus, for obtaining hydrogen chloride	1
		Bottle, wash	1
		Flask, safety	1
		Funnel, separatory	1
		Flask, Würtz (100 ml)	1
		Thermometer	1
		Condenser, air	1
		Receivers	2

Yields are low when ethyl oxalate is obtained by heating oxalic acid with alcohol and sulphuric acid because oxalic acid decomposes when it is heated with sulphuric acid, forming carbon monoxide and dioxide as well as formic acid. Therefore, it is better to use hydrogen chloride as a catalyst and water absorber.

Assembly

1. A 150-ml round-bottom, short-necked flask, placed in a cooling bath, is fitted with a still head, into the straight arm of which a right-angled glass gas tube is inserted almost to the bottom of the flask. A reflux condenser is connected to the side arm of the adapter, and the upper end of the condenser is closed by a calcium chloride tube. A gas tube is connected consecutively by rubber tubings to an empty safety flask and a wash bottle containing concentrated sulphuric acid, and then to the apparatus for obtaining hydrogen chloride.

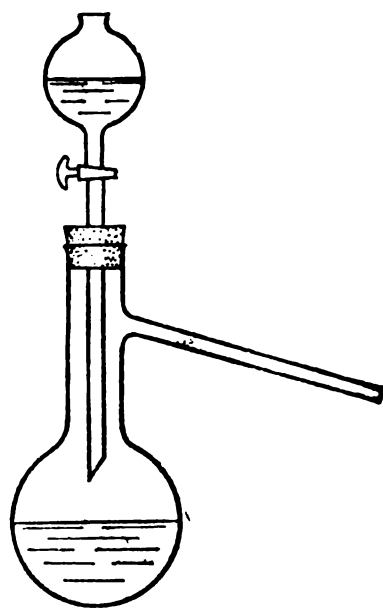


Fig. 9.1. Apparatus for obtaining hydrogen chloride

Hydrogen chloride can be obtained in the Kipp generator under the action of concentrated sulphuric acid on large pieces of fused ammonium chloride. Moreover, it is convenient to obtain hydrogen chloride in the apparatus shown in Fig. 9.1, adding concentrated sulphuric acid dropwise from a dropping funnel to concentrated hydrochloric acid. Hydrogen chloride is dried by passing it through a wash bottle containing concentrated sulphuric acid. It is necessary to put an empty safety flask behind the wash bottle.

This precludes the ejection of the liquid being saturated from the receiver to the wash bottle containing sulphuric acid.

2. A 100-ml Würtz flask is fitted with a thermometer and connected to an air condenser, whose end is lowered into a receiver.

Procedure

Thirty grams of powdered anhydrous oxalic acid (**caution:** oxalic acid *irritates* the skin and the mucous membranes of the respiratory tracts!) are put in the round-bottom, short-necked flask of apparatus 1, 45 ml of absolute ethyl alcohol (see Chap. 2) are added and a strong stream of dry hydrogen chloride is passed through the mixture. In this case, the reaction mixture becomes intensely heated. It is then cooled to 0°C after HCl is passed through it for 10 min.

Anhydrous oxalic acid is obtained from the commercial crystalline $[(\text{COOH})_2 \cdot 2\text{H}_2\text{O}]$ which is ground to powder, put in a porcelain dish and dried for several hours in a drier at 95°C .

Hydrogen chloride is passed through at 0°C until it is no longer absorbed and comes out of the calcium chloride tube, and also until all the oxalic acid dissolves. Afterwards, the contents of the flask are poured gradually, while stirring, on a mixture of 225 g of crushed ice and 100 g of ground crystalline sodium carbonate. The ester isolated is separated in a separatory funnel, washed with a small amount of water, dried by calcium chloride and distilled from the Würtz flask at 186°C .

An emulsion which does not separate into layer for a long time is occasionally formed, impeding the separation of the ethyl oxalate layer. The mixture is then poured into a separatory funnel and extracted twice or three times by ethyl ether (30 ml every time). The combined ester extracts are washed with water and dried by calcium chloride. Ethyl ether is then driven off in a water bath and ethyl oxalate is distilled. The yield of ethyl oxalate is about 24 g.

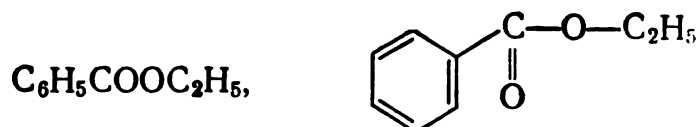
Ethyl oxalate is a colourless liquid with a faint, pleasant odour, slightly soluble in water, and miscible with alcohol and ethyl ether. Its molecular weight is 146.1; b.p., 185.4°C ; m.p., -40.6°C ; d_4^{20} , 1.0785; and n_D , 1.4101.

It is used as a solvent for cellulose esters and ethers and is employed in organic synthesis, for instance, it can be used for obtaining oxalacetic ester. Ethyl oxalate irritates the skin and the mucous membranes of the respiratory tracts.

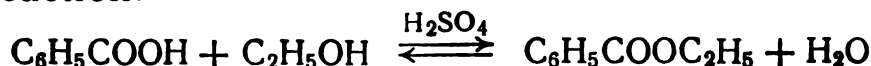
Characterization Test. Sodium oxalate is formed when a weakly alkaline solution of ethyl oxalate is boiled, and it is detected by the formation of a precipitate with calcium salts (after acidifying the solution by acetic acid).

ETHYL BENZOATE

Formula:



Main reaction:



Reagents and Equipment

Benzoic acid	12.2 g (0.1 mole)	Flask, round-bottom (150 ml) . . .	1
Ethyl alcohol, 95 per cent . .	35 ml (0.6 mole)	Condenser, Liebig	1
Sulphuric acid ($d = 1.84$) . . .	4 ml	Funnel, separatory	1
Sodium carbonate		Flask, Würtz (50 ml)	1
Ethyl ether		Thermometer	1
Calcium chloride		Adapter, bent	1
		Condenser, air	1
		Beaker	1
		Receivers	2

Assembly

1. A 150-ml round-bottom flask is connected to a reflux water condenser and placed in a water bath.
2. A 150-ml round-bottom flask placed in a water bath is fitted with a thermometer and a Liebig condenser having a bent adapter whose end is lowered into a receiver.
3. A thermometer is inserted into the neck of a 50-ml Würtz flask, while the side arm is connected to the downflow water condenser with a bent adapter lowered into an ice-cooled receiver. The flask is put in a water bath.
4. A 50-ml Würtz flask is fitted with a thermometer and a short downflow air condenser having a bent adapter lowered into a receiver.

Procedure

Put 12.2 g of benzoic acid (**caution:** benzoic acid *irritates the skin*) and 35 ml of 95 per cent ethyl alcohol in a 150-ml round-bottom flask, and add 4 ml of concentrated sulphuric acid. The mixture is heated in a water bath (apparatus 1) for three or four hours. After the reaction, excess ethyl alcohol is driven off (apparatus 2).

To shift equilibrium to the right, a considerable excess of ethyl alcohol must be taken because ethyl benzoate, which has a high boiling point, is difficult to separate from the reaction sphere and the ethyl alcohol used is not absolute.

The residue is cooled and poured into a beaker containing 60 ml of cold water so that the remaining alcohol and benzoic acid will dissolve. Sodium carbonate is added in portions until a mildly alkaline reaction occurs.

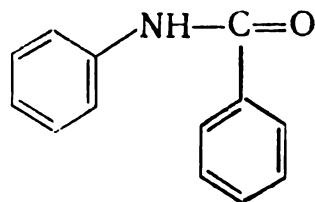
Benzoic acid is extracted by ethyl ether, while the sodium benzoate (formed when sodium carbonate is added) is not extracted. Therefore, it is necessary to see whether the medium is alkaline when sodium carbonate is being added.

Ethyl benzoate which is isolated as an oil is extracted by ethyl ether. The ethereal layer is separated in a separatory funnel and dried by calcium chloride for several hours. After ether is driven off (apparatus 3), residual ethyl benzoate is distilled (apparatus 4) and the fraction which boils at 210-212 °C is collected. The yield of ethyl benzoate is about 10 g.

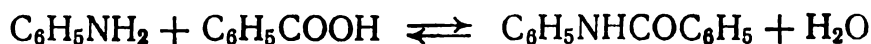
Ethyl benzoate is a colourless liquid with a fruity odour, insoluble in water, but miscible with alcohol, ether and chloroform. Its molecular weight is 150.17; b.p., 212.4 °C; m.p., -34.7 °C; d_4^{15} , 1.0511; and n_D^{20} , 1.5029.

BENZANILIDE

Formula:



Main reaction:

**Reagents and Equipment**

Benzoic acid	16.7 g (0.13 mole)	Flask, round-bottom (150 ml) . . .	1
Aniline	18.6 g or 18 ml (0.2 mole)	Condenser, Liebig	1
Hydrochloric acid, 1 N solution	250 ml	Flask, Bunsen	1
Sodium hydroxide, 1 N solution	250 ml	Funnel, Büchner	1
		Flask, safety	1
		Dish, porcelain	1
		Beaker	1
		Mortar	1
		Receivers	2

Assembly

1. A 150-ml round-bottom flask is connected to a Liebig condenser with a bent adapter whose end is lowered into a receiver. The flask and a thermometer are put in an oil bath.

2. Suction apparatus (see Fig. 2.21).

Procedure

Thirteen millilitres of aniline (caution: aniline is *poisonous*) and 16.7 g of benzoic acid are put in the round-bottom flask of apparatus 1 and the mixture is heated at 180-190 °C until aniline and water cease to be driven off. The temperature is then raised to 225 °C and is maintained at this level until the end of distillation. The oil bath is removed and the flask is allowed to cool slightly, and then another 5 ml of aniline are added and heating is repeated in the same way as described above.

After aniline and water are driven off, the contents of the flask are poured into a porcelain dish. The cooled and solidified product is ground in a mortar and transferred to a beaker, where it is mixed with 125 ml of 1 N hydrochloric acid solution. The liquid over the precipitate is decanted and the foregoing operation is repeated so as to remove unreacted aniline from the precipitate. The product is then washed in the same way with water, twice with 1 N sodium hydroxide solution to remove unreacted benzoic acid, and then several times with water again.

After washing, the precipitate is sucked off on the Büchner funnel and dried, at first in air and then in a drier at 100 °C. The yield of crude benzanilide is about 16 g.

Crude benzanilide can be purified by crystallization from ethyl alcohol by adding activated charcoal.

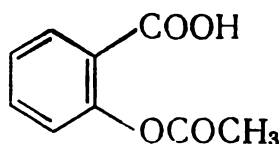
Benzanilide is a colourless crystalline substance soluble in alcohol, ether and benzene, and insoluble in water. Its molecular weight is 197.23; b.p., 117-119 °C at 10 mm Hg; m.p., 163 °C, and d_4^{20} , 1.3200.

It is used as a plasticizer in the paint and varnish industry.

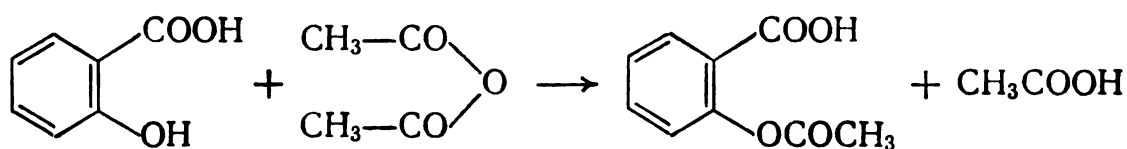
Characterization Test. Benzanilide turns the quinone solution red, and the solution of potassium chromate in sulphuric acid, violet.

ASPIRIN (ACETYLSALICYLIC ACID)

Formula:



Main reaction:



Preparation of Aspirin by the Direct Action of Acetic Anhydride on Salicylic Acid

Reagents and Equipment

Salicylic acid	12.5 g (0.09 mole)	Flask, round-bottom (100 ml) . . .	1
Acetic anhydride	10.2 g or 10 ml (0.1 mole)	Condenser, air	1
Sulphuric acid ($d = 1.84$)	0.5 ml	Tube, calcium chloride	1
Toluene		Beaker (300 ml)	1
		Funnel, Büchner	1
		Flask, Bunsen	1
		Flask, safety	1
		Thermometer	1

Assembly

1. A 100-ml round-bottom flask is connected to a reflux air condenser fitted with a calcium chloride tube and is placed in a water bath.

2. Suction apparatus (see Fig. 2.21).

Procedure

Put 12.5 g of salicylic acid, 10 ml of acetic anhydride (**caution:** acetic anhydride is *flammable* and irritates the skin) and 0.5 ml of concentrated sulphuric acid in the round-bottom flask of apparatus 1. The mixture is heated (apparatus 1) in a water bath at 60°C for one hour. Afterwards, the temperature is raised to 90–95°C and the reaction mixture is kept at this temperature for 20 min. The liquid is then allowed to cool while stirring. After cooling, the liquid is poured into 20 ml of water and stirred. The aspirin isolated is sucked off on the Büchner funnel and washed with a small amount of cold toluene. The aspirin yield is about 16 g.

To purify aspirin, it can be recrystallized out of dilute (1 : 1) acetic acid, benzene, chloroform or ethyl alcohol.

Preparation of Aspirin under the Action of Acetic Anhydride on Salicylic Acid in a Solvent Medium

Reagents and Equipment

Salicylic acid	12.5 g (0.09 mole)	Flask, round-bottom (100 ml) . . .	1
Acetic anhydride	10 g or 9 ml (0.1 mole)	Condenser, water	1
Benzene, anhydrous	30 ml	Tube, calcium chloride	1
		Funnel, hot filtration	1
		Funnel, Büchner	1
		Dish, porcelain	1
		Flask, Bunsen	1
		Flask, safety	1
		Thermometer	1

Assembly

1. A 100-ml round-bottom flask is connected to a reflux water condenser (without circulation of water or with its slight circulation) fitted with a calcium chloride tube and is placed in a water bath.

2. Suction apparatus (see Fig. 2.21).

Procedure

Fifteen millilitres of dry benzene (benzene should be dried by calcium chloride), 12.5 g of dry salicylic acid and 9 ml of freshly distilled acetic anhydride (acetic anhydride is distilled over anhydrous sodium acetate) are put in the round-bottom flask of apparatus 1 and the mixture is heated in a boiling water bath (apparatus 1) for four hours, shaking the flask from time to time. The reaction liquid is then tested for the presence of salicylic acid which, with an aqueous ferric chloride solution, produces the characteristic violet colour.

If salicylic acid is not detected, the contents of the flask are passed through a fluted filter on the hot filtration funnel and the filtrate is left in a porcelain dish for one day.

On the next day, the dish is put for 30 min in a cooling bath (the temperature ranges from -5°C to -10°C); afterwards, the aspirin which has precipitated is sucked off on the Büchner funnel, washed with dry benzene cooled to 6°C until the odour of acetic acid disappears, and dried. The filtrate can be used for extracting aspirin which remains in the solution.

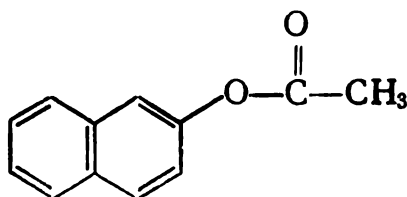
First, benzene is distilled from the filtrate with a condenser by heating the mixture in a water bath. Then, acetic acid and acetic anhydride are driven off under vacuum (20 mm Hg). The aspirin yield is about 13 g.

Aspirin (acetylsalicylic acid) consists of needles or flakes of colourless crystals with a slightly bitter taste; it dissolves sparingly in water and well in aqueous alkaline solutions. Its molecular weight is 180.16 and m.p., 136.5°C . It is widely used in medicine as an antipyretic and an analgesic.

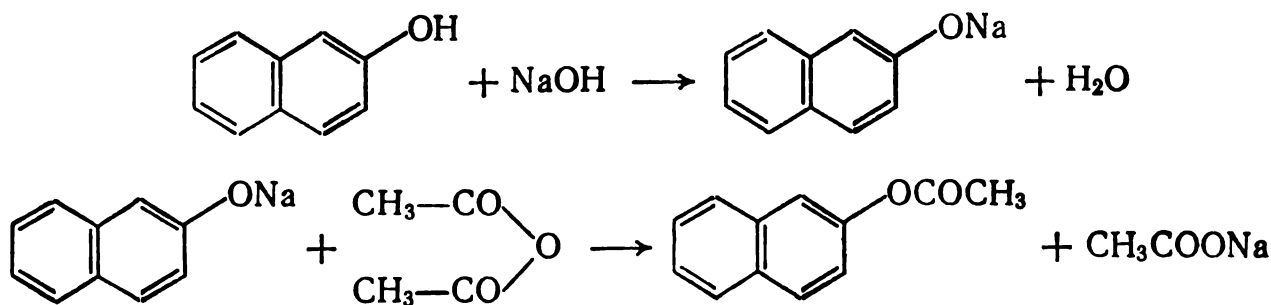
Characterization Test. When aspirin is heated with alkalies, it decomposes into salicylic and acetic acids.

β -NAPHTHYL ACETATE

Formula:



Main reactions:



Reagents and Equipment

β -Naphthol . . . 10 g	(0.07 mole)	Flask, round-bottom (500 ml) . . . 1
Acetic anhydride . 11.4 g	or 10.5 ml	Condenser, air 1
Sodium hydroxide 5 g	(0.11 mole)	Funnel, Büchner 1
Ice		Flask, Bunsen 1
		Flask, safety 1

Assembly

1. A 500-ml round-bottom flask is connected to a reflux air condenser.
2. Suction apparatus (see Fig. 2.21).

Procedure

Ten grams of pure β -naphthol are dissolved in 50 ml of a 10 per cent sodium hydroxide solution in a 500-ml round-bottom flask.

β -Naphthol can be purified by recrystallization from water with dilute ethyl alcohol or from carbon tetrachloride.

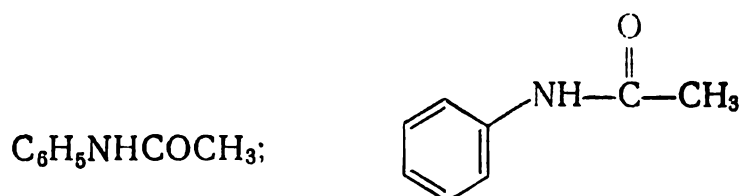
Add 125 g of crushed ice and 10.5 ml of acetic anhydride to the solution. The flask is shaken for 15-20 min (apparatus 1). The β -naphthyl acetate which has precipitated is sucked off on the Büchner funnel, washed with water and dried in air. The yield of β -naphthyl acetate is about 13 g.

To purify β -naphthyl acetate, it is recrystallized from dilute ethyl alcohol.

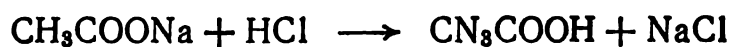
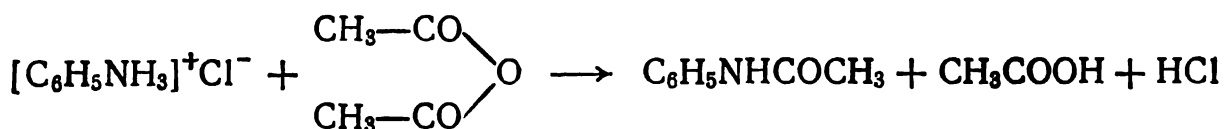
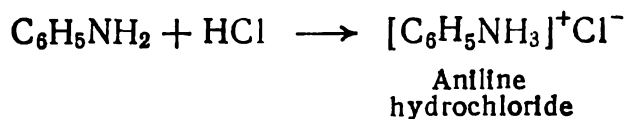
β -Naphthyl acetate is a colourless crystalline substance which melts at 71 °C. It dissolves well in ether and chloroform. It is used in organic synthesis.

ACETANILIDE

Formula:



Main reactions:



Reagents and Equipment

Aniline	9.3 g or 9 ml (0.1 mole)	Beaker (500 ml)	1
Acetic anhydride	12.5 ml (0.13 mole)	Stirrer	1
Hydrochloric acid ($d = 1.19$) .	8.5 ml (0.1 mole)	Funnel, Büchner	1
Sodium acetate, crystalline .	15 g	Flask, Bunsen	1
		Flask, safety	1
		Thermometer	1

Assembly

1. A 500-ml beaker fitted with a stirrer is placed in a water bath.
2. Suction apparatus (see Fig. 2.21).

Procedure

Pour 8.5 ml of concentrated hydrochloric acid into a beaker containing 250 ml of water, and add 9 ml of freshly distilled aniline while stirring the mixture with a stirrer.

The colourless solution is heated in a water bath to 50°C, 12.5 ml of acetic anhydride are added and the mixture is stirred (*caution: there may be an ejection*).

If the solution is coloured, two grams of activated charcoal are added and the mixture is stirred for several minutes and filtered off.

Afterwards, a solution of 15 g of sodium acetate in 50 ml of water is added, and the mixture is stirred well and cooled with ice. The acetanilide crystals which have fallen out are sucked off on the Büchner funnel, washed with ice water and dried. Acetanilide can be recrystallized from water. The acetanilide yield is about 10 g.

Acetanilide (phenylacetamide) is a white, odourless, crystalline substance which dissolves sparingly in cold water and well in ether, alcohol, chloroform, acetone and aniline.

It is used as an antipyretic and an analgesic in medicine, and as an intermediate in dye synthesis. It is also employed as a hydrogen peroxide stabilizer.

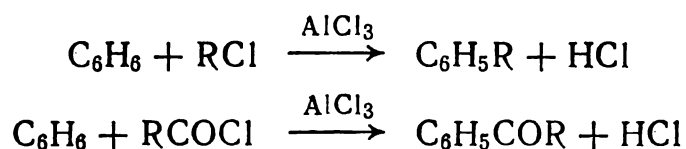
Characterization Test. Heat 0.2 g of acetanilide and 1 ml of hydrochloric acid for two minutes, and then add a small phenol crystal, 5 ml of water and 2 ml of chlorinated lime; the mixture becomes dirty violet. When an excess of ammonia is added to the mixture, the colour changes to dark blue (indophenol reaction).

Chapter 10

FRIEDEL-CRAFTS REACTIONS

In 1877, C. Friedel and J. Crafts showed that benzene and its homologues are capable of being alkylated under the action of alkyl halides in the presence of anhydrous aluminium chloride. In this case, hydrogen chloride is eliminated and the hydrogen atom of the aromatic ring is replaced by the appropriate radical. It was later ascertained that this reaction is possible for the most diverse aromatic compounds: benzene and its homologues and derivatives, naphthalene and its derivatives, several heterocyclic compounds, etc.

At present, the Friedel-Crafts reaction implies the alkylation or acylation of aromatic compounds by alkyl or acyl halides in the presence of special catalysts, e.g., anhydrous aluminium chloride:



The first reaction is used mainly for obtaining alkylated aromatic hydrocarbons. The second reaction, being of great importance, is the best method of obtaining aromatic ketones.

In most cases, the Friedel-Crafts reaction is carried out in the presence of aluminium chloride, but sometimes use is also made of other catalysts (FeCl_3 , BF_3 , ZnCl_2 , H_2SO_4 , H_3PO_4) whose activity depends on the nature of the alkylating agent.

Aluminium chloride is usually used as a finished solid product (powder). In this case, it must be pure and dry. It is expedient to purify aluminium chloride by sublimation before using it. Aluminium chloride can be obtained also in the reaction vessel when metallic aluminium reacts with the hydrogen chloride gas (Radzivanovsky catalyst).

10.1. ALKYLATION OF AROMATIC COMPOUNDS

Some aromatic compounds can be readily alkylated in the presence of aluminium chloride by alkyl halides, olefins and alcohols. The reaction rate depends on the nature of the halogen and the agent being alkylated.

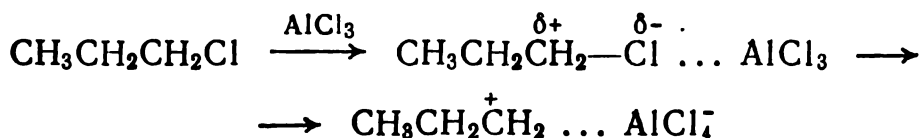
In the laboratory, alkylation by the Friedel-Crafts method is of limited importance. For instance, a mixture of mono-, di- and poly-substituted hydrocarbons is obtained when benzene is alkylated, because the rate of alkylation of benzene itself is less than that of the alkyl benzene which is formed at the initial stage. Not only is hydrogen of the aromatic ring replaced by the alkyl radical, but also the products may be dehydrogenated, hydrogenated, isomerized

and polymerized under the action of aluminium chloride. Benzene alkylation can be partially controlled by taking the appropriate amounts of reagents. If a monoalkyl-substituted product of benzene is to be obtained, a large excess of the latter is taken. If polyalkyl-substituted derivatives of benzene are to be obtained, an excess of the alkylating agent is taken. A certain amount of products of a different degree of substitution is, however, inevitably formed, thus reducing the yield and giving rise to definite difficulties in isolating the main product.

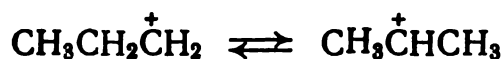
Derivatives having a branched side chain can be formed when aromatic compounds react with primary alkyl halides, which have an unbranched chain of carbon atoms. For instance, isopropylbenzene is obtained from benzene and *n*-propyl chloride, and *sec*-butylbenzene, from *n*-butyl bromide and benzene.

Alkylation in the presence of aluminium chloride can be represented in the following way, taking the example of isopropylbenzene formation.

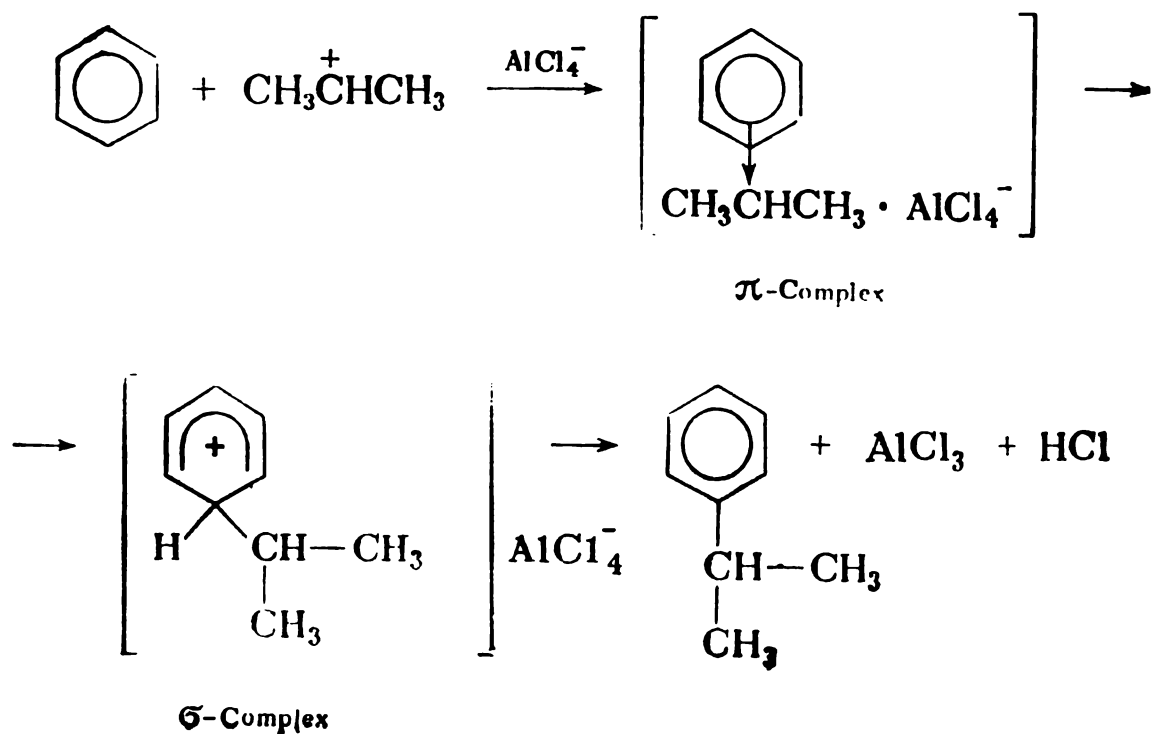
In anhydrous aluminium chloride, the aluminium atom has only six electrons on the outer orbital. It fills up this group to an octet by drawing out chlorine electrons of propyl chloride:



The carbonium ion $\text{CH}_3\text{CH}_2\overset{+}{\text{CH}_2}$ is isomerized into a more stable ion:



It is this ion which is an electrophilic alkylating agent:



Before carrying out synthesis by the Friedel-Crafts method, all the reagents should be thoroughly dried, because aluminium chloride and other catalysts of this reaction are readily hydrolyzed. The apparatus for carrying out the reaction should also be dried and protected from moisture.

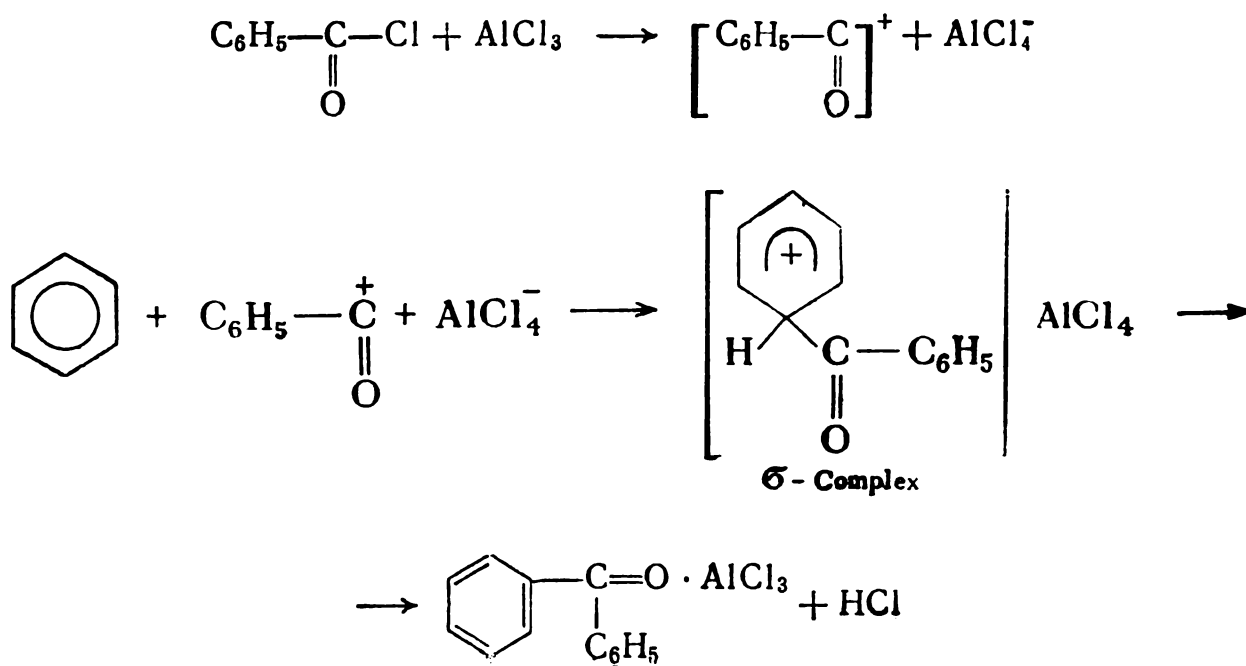
10.2. ACYLATION OF AROMATIC COMPOUNDS

Acylation of aromatic hydrocarbons by the Friedel-Crafts method is a very important method of synthesizing ketones of a different structure because the introduction of the carbonyl group into the molecule of an aromatic compound impedes further acylation, resulting in the formation of homogeneous reaction products with high yields. The acylating agents used are chlorides of fatty and aromatic acids, acid anhydrides, phosgene and carboxylic acids.

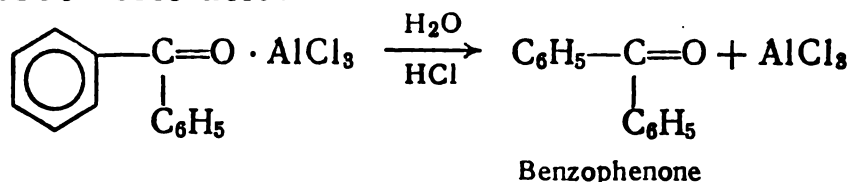
The catalyst is selected in conformity with the reactivity of an aromatic compound. Aluminium chloride is used in most cases, while zinc chloride, sulphuric acid and others are used only for highly reactive substances (e.g., thiophene).

Unlike alkylation by the Friedel-Crafts method, for which the presence of a small amount of aluminium chloride is enough, acylation occurs satisfactorily only when the amount of aluminium chloride used is far greater than that used for obtaining alkyl benzenes. This is due to the formation of a complex compound of aluminium chloride and oxygen-containing reagents, such as acid chlorides, acid anhydrides, ketones and acids.

For instance, the formation of diphenyl ketone can be represented by the following scheme:



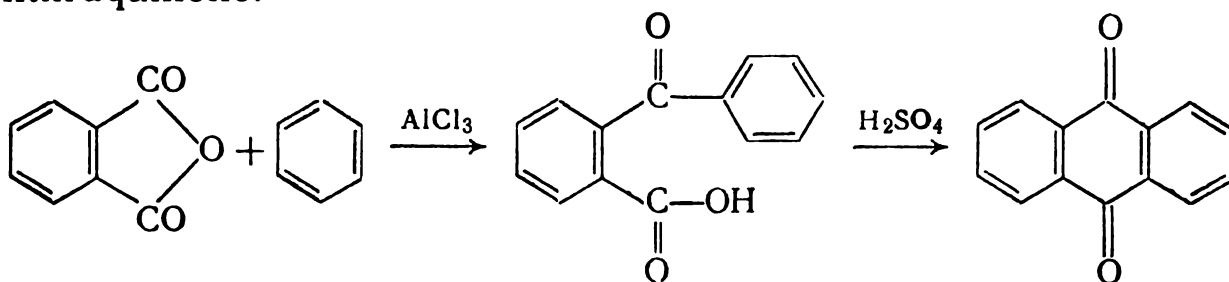
The complex obtained is decomposed by ice water in the presence of hydrochloric acid:



Benzophenone which is dissolved in an organic solvent rises to the surface. Aluminium chloride remains in the aqueous solution.

Aluminium chloride which is bound with ketone does not participate in the reaction. Therefore, the amount of it used should be such that a certain excess, needed as a catalyst for acylation by the Friedel-Crafts method, will be left after complex formation. In acylation by acid anhydrides, an even larger amount of aluminium chloride must be used because the ketone and acetic acid, formed as a result of the reaction, bind the same amount of the catalyst. Therefore, in ketone synthesis, use more than 1 mole of aluminium chloride per mole of acid chloride, and more than 2 moles of aluminium chloride per mole of acid anhydride.

The interaction with the anhydrides of dibasic carboxylic acids is especially interesting. In this case, keto acids are formed, and they can subsequently be converted into diketones. For example, *o*-benzoyl-benzoic acid (*o*-carboxybenzophenone) is formed from phthalic anhydride and benzene, and can then be condensed to anthraquinone:



Acylation by the Friedel-Crafts method can be applied to mono- and polynuclear aromatic hydrocarbons, monoalkyl and polyhalogen derivatives of benzene, phenol ethers, and reactive heterocycles (e.g., thiophene and furan). Nitro compounds and phenols do not enter into this reaction.

The selection of a solvent for the Friedel-Crafts synthesis is rather limited because very many organic compounds react with aluminium chloride. The solvent used is mainly excess aromatic hydrocarbon as well as carbon disulphide, nitrobenzene and petroleum ether.

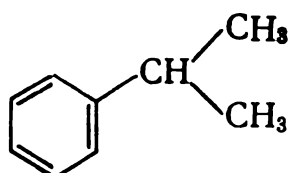
The technique of carrying out acylation does not differ in the main from that of carrying out alkylation. The interaction between aromatic compounds and acylating agents is also an exothermic reaction. Therefore, an acid chloride or anhydride should be added

dropwise to the mixture. After the acylating agent is added, the reaction mixture is heated in a water bath for 1-3 h, and then poured out on ice and treated with hydrochloric acid. The ketone isolated is extracted by a solvent, the water layer is separated, and then the ketone is dried and distilled.

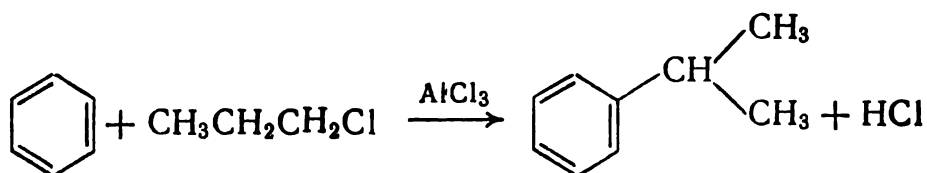
10.3. SYNTHESSES

ISOPROPYLBENZENE

Formula:



Main reaction (for the reaction mechanism, see p. 183):



Reagents and Equipment

Benzene	100 g or 114 ml (1.28 mole)	Flask, Würtz (200 ml)	1
Propyl chloride	10 g or 11 ml (0.12 mole)	Flask, round-bottom (300 ml)	1
Aluminium chloride, anhydrous	2 g	Head, still	1
Sodium hydroxide		Condenser	1
Magnesium sulphate		Tube, calcium chloride	1
Ice		Funnel, dropping	1
Hydrochloric acid		Funnel, separatory	1
		Flask, conical	1
		Thermometer	1
		Beaker	1

Assembly

1. A 300-ml round-bottom flask is placed in a water bath and connected by a still head to a dropping funnel and a reflux water condenser, fitted with a calcium chloride tube, to whose outer end a bent glass tube is connected and lowered into a water-containing flask so as to absorb hydrogen chloride. The end of the tube should be about 1 cm away from the water surface; otherwise, water may be drawn into the apparatus. A thermometer is put in the water bath.

2. A 200-ml Würtz flask with a downflow water condenser.

Procedure

Eighty millilitres of thiophene-free dry benzene and two grams of anhydrous, thoroughly ground aluminium chloride (caution: aluminium chloride *irritates the skin*, and its dry preparation

causes an *explosion* when it reacts with water!) are put in a round-bottom flask of apparatus 1.

1. Crude benzene contains about 0.15 per cent of thiophene. To purify benzene from thiophene, one litre of benzene is mixed with 80 ml of concentrated sulphuric acid and vigorously stirred for 30 min. The dark, sulphuric acid layer formed is separated and the mixture with sulphuric acid is stirred again until the acid is almost colourless. Benzene is then carefully driven off.

To dry benzene, it is distilled and the first 10 per cent of the distillate is discarded. All the moisture is driven off as an azeotropic mixture with benzene.

2. All the operations involving anhydrous aluminium chloride should be carried out as rapidly as possible because it is highly hygroscopic.

A solution of 11 ml of propyl chloride in 34 ml of benzene is added dropwise to the flask while maintaining the temperature of the reaction mixture at about 80°C (*m*-diisopropylbenzene is formed when the temperature is higher and when large amounts of aluminium chloride are used).

After all the propyl chloride has been added, heating is continued until hydrogen chloride is no longer liberated.

The end of the reaction is determined by: (a) the absence of red colour on blue litmus paper and (b) the absence of fumes when a test tube containing ammonia is brought to the end of the bent glass tube or when the hydrogen chloride liberated is passed through a preliminarily weighed flask containing water. The reaction is stopped when the calculated amount of hydrogen chloride is absorbed.

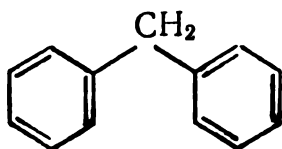
The reaction mixture is then poured on ice, aluminium hydroxide is dissolved by hydrochloric acid, the upper layer of isopropylbenzene in the benzene solution is separated in a separatory funnel and washed with a dilute solution of sodium hydroxide and water until the solution reacts neutral. Afterwards, it is dried by magnesium sulphate or calcium chloride and fractionated (apparatus 2), collecting the isopropylbenzene fraction at 151-153°C. The isopropylbenzene yield is about 11 g.

Isopropylbenzene (cumene) is a colourless, water-insoluble liquid which mixes with alcohol, ether, acetone, chloroform and benzene. Its molecular weight is 120.19; b.p., 152.4°C; m.p., -96.03°C; d_4^{20} , 0.8618; and n_D^{20} , 1.4913. It is highly flammable (its flash point is 38°C) and forms explosive vapour-air mixtures.

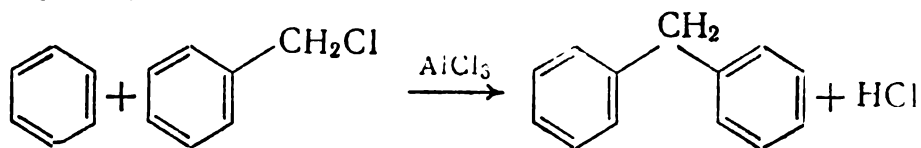
It is used as a solvent of lacquers and paints and as an additive to aviation fuel. It is also employed in the production of phenol and acetone.

DIPHENYLMETHANE

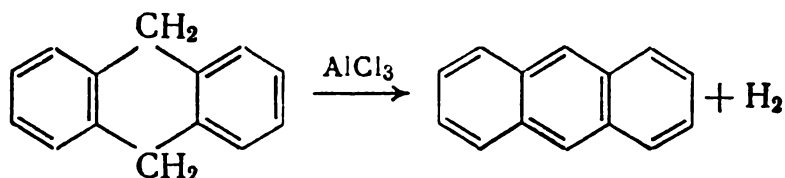
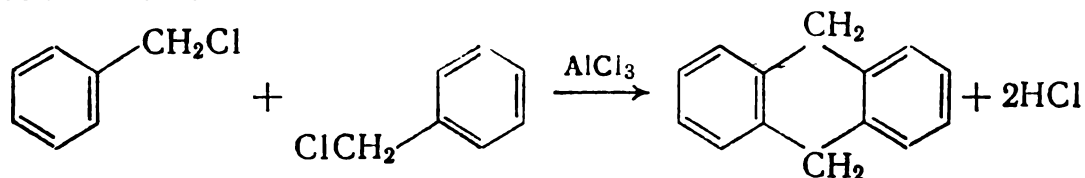
Formula:



Main reaction:



Side reactions:



Reagents and Equipment

Benzene	43 g or 50 ml (0.56 mole)	Flask, round-bottom, two-necked (200 ml)	1
Benzyl chloride	12.7 g or 12 ml (0.1 mole)	Condenser, Liebig	1
Aluminium chloride, an- hydrous	5 g	Tube, calcium chloride	1
Hydrochloric acid ($d = 1.19$)		Funnel, dropping	1
Sodium hydroxide		Funnel, separatory	1
Ice		Flask, conical	1
		Flask, Würtz (100 ml)	1
		Thermometer	1
		Adapter, bent	1
		Receivers	2

Assembly

1. A 200-ml round-bottom, two-necked flask is fitted with a dropping funnel and a reflux water condenser having a calcium chloride tube, which is connected to a bent glass tube whose end is lowered into a flask with water (about 1 cm above the water surface). The apparatus is put *in a fume cupboard!*

2. A Würtz flask placed in a water bath is fitted with a thermometer and a Liebig condenser having a bent adapter, which is lowered into a receiver.

Procedure

Fifty millilitres of dry benzene and 5 g of thoroughly ground anhydrous aluminium chloride are put in the round-bottom, two-necked flask of apparatus 1 (see p. 186); 12 ml of benzyl chloride are then added dropwise (work with benzyl chloride must be done *in a fume cupboard* because its vapours are *lachrymatory and irritate the respiratory tracts!*)

When hydrogen chloride is no longer liberated, 40 g of crushed ice and some hydrochloric acid are put in the flask. The reaction

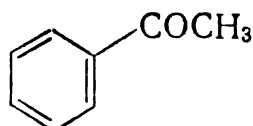
mixture is transferred to a separatory funnel and the upper benzene layer containing diphenylmethane is separated. It is then washed with water and a sodium hydroxide solution, and again with water until the solution reacts neutral. After driving off benzene from the benzene solution (apparatus 2), the condenser is removed, the outlet tube of the Würtz flask is put in a receiver, which is in a dish containing cold water, and diphenylmethane is driven off in the Babo funnel (p. 35). If diphenylmethane is coloured or does not solidify on cooling, it should be redistilled with two or three pieces of metallic sodium. The diphenylmethane yield is about 10 g.

Diphenylmethane consists of colourless crystals with an odour like orange peel; it does not dissolve in water, but does dissolve well in alcohol, ether, chloroform and benzene. Its molecular weight is 168.5; b.p., 261-262 °C; m.p., 26-27 °C; d_4^{20} , 1.0060; and n_D^{20} , 1.5788.

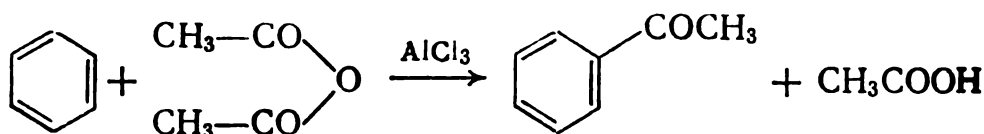
It is used as a solvent of lacquers and dyes, and also for soap fragrance.

ACETOPHENONE

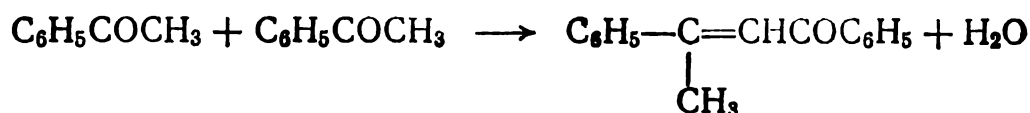
Formula:



Main reaction:



Side reaction:



Reagents and Equipment

Benzene, anhydrous	35 g or 40 ml (0.45 mole)	Flask, round-bottom, three-necked (300 ml)	1
Acetic anhydride	10.2 g or 10 ml (0.1 mole)	Stirrer, mechanical	1
Aluminium chloride, anhydrous	32 g (0.24 mole)	Condenser, Liebig	1
Diethyl ether	35 ml	Funnel, dropping	1
Sodium hydroxide, 10 per cent	25 ml	Funnel, conical	1
Hydrochloric acid, 10 per cent		Funnel, separatory	1
Calcium chloride, anhydrous		Tubes, calcium chloride	2
		Beakers	2
		Flask, Würtz (100 ml)	1
		Thermometers	2
		Adapter	1
		Condenser, air	1
		Receiver	1

Assembly

1. A 300-ml round-bottom, three-necked flask (or a round-bottom flask with a still head) is placed in a water bath and fitted with a stirrer, a dropping funnel and a reflux water condenser. The condenser and the dropping funnel are closed with calcium chloride tubes. A bent glass tube, attached to an inverted glass funnel, is connected to the outer end of the condenser's calcium chloride tube. The funnel is then so lowered into a beaker containing water that its rim is about 1 cm away from the water surface. A thermometer is put into the water bath (Fig. 10.1).

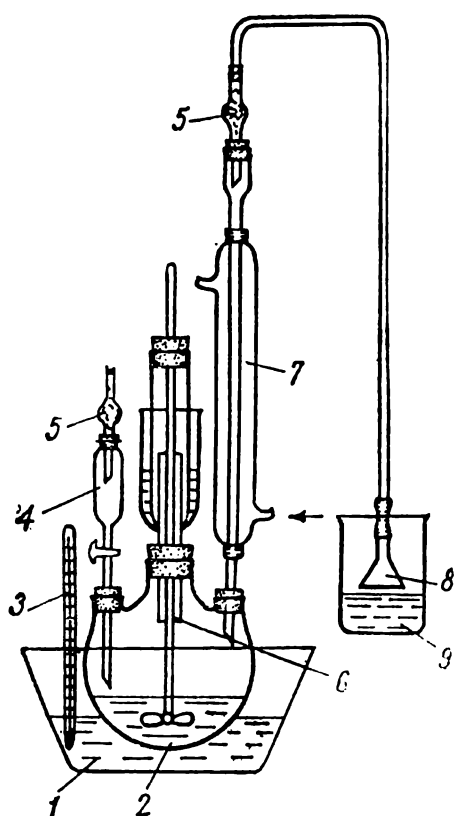
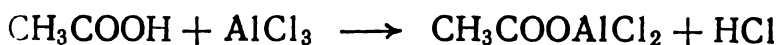


Fig. 10.1. Apparatus for obtaining acetophenone:

1—water bath; 2—round-bottom, three-necked flask; 3—thermometer; 4—dropping funnel; 5—calcium chloride tube; 6—stirrer; 7—condenser; 8—funnel; 9—beaker

The acetic acid formed as a result of the reaction reacts with aluminium chloride:



The hydrogen chloride being liberated must be absorbed with water.

2. A 250-ml Würtz flask is placed in a water bath and fitted with a thermometer and a Liebig condenser having a bent adapter, whose end is lowered in a receiver.

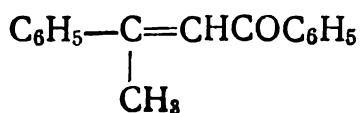
3. A 100-ml Würtz flask is connected to a thermometer and a down-flow air condenser.

The entire apparatus should be thoroughly dried, since aluminium chloride is hygroscopic.

Procedure

Acetophenone vapours should not be inhaled because they are *soporific*.

Forty millilitres of dry benzene (see p. 186) and 32 g of finely ground, freshly distilled aluminium chloride are put in the round-bottom, three-necked flask of apparatus 1. The stirrer is switched on and while cooling the flask with cold water, 10 ml of pure acetic anhydride are added dropwise for 30 min through a dropping funnel (see p. 189). To complete the reaction, the flask is heated in a water bath at 80-85 °C for 45 min. If it is heated any longer, the acetophenone yield will diminish due to the formation of a high-boiling product, dyprnone



The cooled reaction mixture is poured into a beaker containing 80 g of water with ice. If basic aluminium salt precipitates (in the hydrolysis of a complex compound of aluminium chloride and acetophenone), dilute hydrochloric acid is added until the precipitate dissolves.

The mixture is transferred to a separatory funnel and treated with 20 ml of ethyl ether; the ethereal-benzene layer is then separated, while the water layer is extracted again with 15 ml of ether. The combined ethereal extracts are washed first with water, next with 25 ml of a sodium hydroxide solution, then once again with water and dried with anhydrous calcium chloride.

After the solvents (ether and benzene) have been driven off in a water bath (apparatus 2), acetophenone is distilled (apparatus 3) and the fraction which boils at 199-203 °C is collected. Acetophenone can also be distilled under vacuum (12 mm Hg) at 88 °C. The acetophenone yield is about eight grams.

Acetophenone (phenyl methyl ketone) is a colourless or, occasionally, a yellowish, oily liquid, or sometimes large, readily melting crystals with a bird cherry odour. It dissolves sparingly in water and well in alcohol, ether, chloroform and benzene. Its molecular weight is 120.14; b.p., 202.3 °C at 760 mm Hg or 88 °C at 12 mm Hg; m.p., 20.5 °C; d_4^{20} , 1.0281; and n_D^{20} , 1.5342. It is used in perfumes.

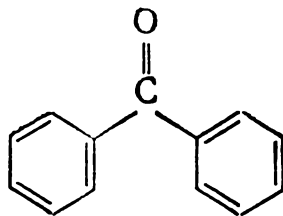
Characterization Tests. 1. Put two drops of acetophenone in 2 ml of a 0.5 per cent sodium nitroprusside solution and add two drops of a 10 per cent sodium hydroxide solution. The solution will turn red. When acetic acid is added, the colour changes to dark blue.

2. Acetophenone dissolves well in concentrated sulphuric acid, producing an orange-yellow colour.

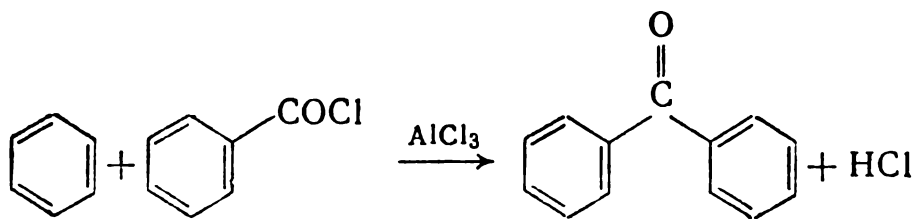
When water is added, acetophenone is separated again.

BENZOPHENONE

Formula:



Main reaction (for the reaction mechanism, see p. 185).



Reagents and Equipment

Benzene, anhydrous	48 g or 55 ml (0.62 mole)	Flask, round-bottom (500 ml)	1
Benzoyl chloride	14 g or 11.5 ml (0.11 mole)	Head, still	1
Aluminium chloride, anhydrous	15 g	Condenser, Liebig	1
Hydrochloric acid ($d = 1.19$)		Funnel, dropping	1
Ethyl ether		Funnel, conical	1
Sodium hydroxide, 5 per cent	25 ml	Tubes, calcium chloride	2
Calcium chloride, granulated		Beaker	1
		Thermometer	1
		Apparatus, steam distillation	1
		Funnel, separatory	1
		Flask, Würtz (100 ml)	1
		Adapter, bent	1
		Thermometer	1
		Flask, Würtz (50 ml) with an out- let tube sealed low	1

Assembly

1. A 50-ml round-bottom flask, placed in a water bath, is connected by a still head to a reflux condenser and a dropping funnel, which are closed with calcium chloride tubes. The calcium chloride tube of the condenser is connected to a bent glass tube, which is attached to an inverted glass funnel so lowered into a beaker containing water that its rim is 1 cm above the water surface. A thermometer is put in the water bath.

2. Steam distillation apparatus (see Fig. 3.6).

3. A 100-ml Würtz flask, placed in a water bath, is connected to a thermometer and Liebig condenser having a bent adapter lowered into a receiver.

Procedure

Fifteen grams of anhydrous, thoroughly ground aluminium chloride (see p. 186) and 55 ml of dry benzene (see p. 186) are put in the round-bottom flask of apparatus 1. Afterwards, add 11.5 ml of benzoyl chloride from a dropping funnel, shaking it to prevent the reaction from occurring too vigorously.

The flask is then heated in a water bath at 50 °C until hydrogen chloride is no longer liberated (this usually takes two or three hours). After cooling, carefully add, while stirring, 150 ml of water, several pieces of ice (for decomposing the complex of benzophenone and aluminium chloride) and some concentrated hydrochloric acid (for transforming basic aluminium salt into solution) to the flask's dark brown contents. Afterwards, benzene is steam distilled (apparatus 2) for 20 min.

The mixture remaining in the flask is cooled and mixed with ether in a separatory funnel. The ethereal extract is washed with 25 ml of an aqueous sodium hydroxide solution and dried with

calcium chloride (calcium chloride can be replaced by anhydrous magnesium sulphate or potassium carbonate), and the ether is driven off (apparatus 3). The residue is distilled under atmospheric pressure from a Würtz flask which has an outlet tube sealed low without a condenser. The fraction which boils at 297 °C is collected. If a product of higher purity is to be obtained, the residue is distilled under vacuum and the fraction which boils at 170-175 °C (15 mm Hg) is collected. The benzophenone yield is about 13 g.

Benzophenone (diphenyl ketone) is a lustrous white, crystalline substance with a peculiar odour. It does not dissolve in water, but it does dissolve in chloroform. Its molecular weight is 182.21. It is known to exist in stable and metastable forms. Its stable form is: b.p., 305 °C; m.p., 48 °C; d_{50}^{50} , 1.0976, and n_D^{15} , 1.5975. Its metastable form is: b.p., 305 °C; m.p., 26 °C; d , 1.108, and n_D^{15} , 1.6060.

The metastable form of benzophenone is usually obtained in distillation. At the moment of distillation, this form is a liquid which, without seeding, very slowly solidifies into colourless crystals. When the vessel side is rubbed or crystals of a stable form are added, the liquid rapidly solidifies, turning into a stable form.

Benzophenone is used in perfumes and dye production as well as for other purposes.

Characterization Tests. 1. It dissolves and produces a yellow colour in concentrated sulphuric acid. Benzophenone is separated again when water is added.

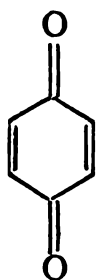
2. A dark blue colour appears when it is carefully fused with metallic sodium.

Chapter 11

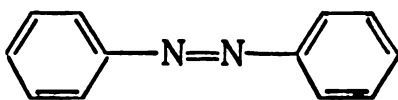
OXIDATION REACTIONS

Oxidation consists of the removal of electrons. The more readily compounds are oxidized, the greater their tendency to give away electrons. Oxidizing agents are substances which have an affinity for electrons.

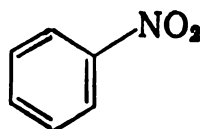
Organic compounds are oxidized, in most cases, by the following oxidizing agents: atmospheric oxygen, potassium permanganate, a chromic acid mixture (obtained by dissolving potassium or sodium bichromate in sulphuric acid), chromic anhydride, nitric acid, ozone, lead oxide, silver oxide, aluminium *tert*-butylate, etc. An oxidizing agent's action on an organic compound depends on the nature of the substance being oxidized and on the chemical nature of the oxidizing agent itself. For instance, benzoquinone is formed when aniline is oxidized by a chromic acid mixture. When oxidized by Berthollet's salt or potassium dichromate in the presence of a catalyst (the salt of vanadium, copper or iron), aniline forms aniline black (a dye of a complex structure). Azobenzene is formed when it is oxidized by potassium permanganate in a neutral medium. Nitrobenzene is formed from the oxidation of aniline by potassium permanganate in an alkaline medium, and *p*-aminophenol, by chloric acid:



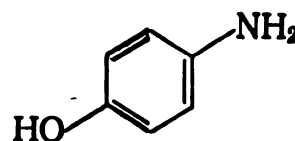
Benzoquinone



Azobenzene

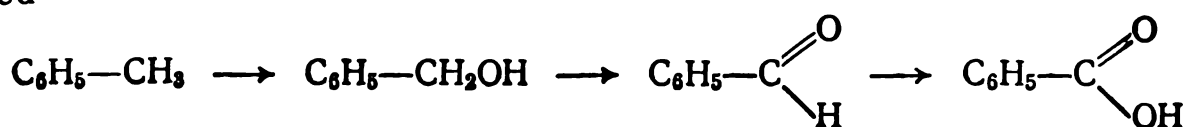


Nitrobenzene



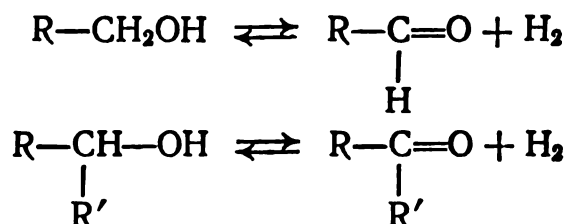
p-Aminophenol

An organic compound's oxidizability is connected with the presence of hydrogen atoms. In oxidation, either they are given away or oxygen atoms are added. For instance, toluene is readily oxidized



while tertiary alcohols $\begin{array}{c} \text{R} \\ | \\ \text{R}-\text{C}-\text{OH} \\ | \\ \text{R} \end{array}$ are oxidized under drastic con-

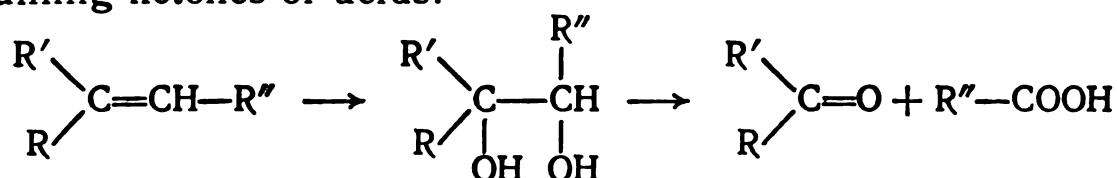
ditions involving the rupture of the carbon chain. One instance of an oxidation reaction is dehydrogenation, the removal of hydrogen. A very important industrial method of obtaining aldehydes and ketones is the catalytic dehydrogenation of primary and secondary alcohols:



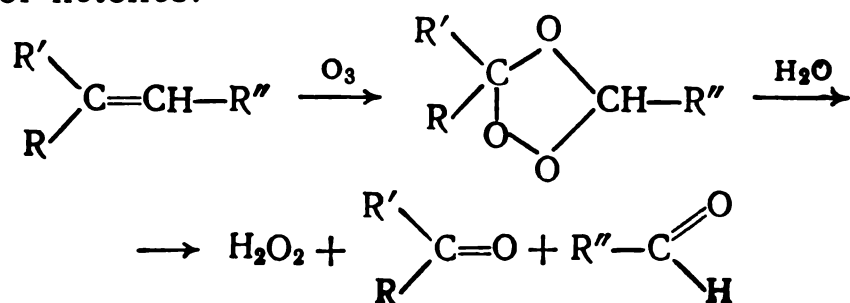
The catalysts used are metallic copper, silver, cupric chromate and zinc oxide. Dehydrogenation is an endothermic process, and the catalyst is therefore constantly heated.

11.1. OXIDATION AT THE DOUBLE BOND

The double bond is very sensitive to the chromic acid mixture and potassium permanganate. Two hydroxyl groups are added at first under the action of an oxidizing agent. The glycol formed is then oxidized further with the cleavage of the carbon bond, thus obtaining ketones or acids:



This reaction is used to obtain glycols, ketones and acids from unsaturated hydrocarbons, and also for determining the structure of unsaturated compounds. To obtain aldehydes and ketones if other methods fail, and also to determine the position of the double bonds and the structure of unsaturated compounds, oxidation at the double bond can be carried out under the action of ozone. Ozone is added across the double bond, forming very unstable, explosive ozonides, which, under the action of water, readily decompose to aldehydes or ketones:



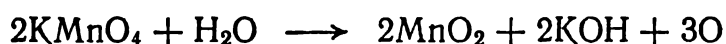
11.2. OXIDATION OF PRIMARY AND SECONDARY ALCOHOLS TO ALDEHYDES OR KETONES

To oxidize primary aliphatic alcohols to aldehydes in the laboratory, a chromic acid mixture, manganese dioxide with sulphuric acid and nitric acid are usually used. The aldehyde being formed is subject to further oxidation to a corresponding acid, thus diminishing the yield of the reaction products. Therefore, the aldehyde produced should be removed from the reaction medium as soon as possible. This is done by (1) slowly adding an oxidizing agent and (2) passing a carbon dioxide stream, which entrains highly volatile aldehyde, through the reaction mixture.

To obtain unsaturated and aromatic aldehydes, use is made, in oxidation, of *tert*-butyl chromate either in petroleum ether or in benzene, and manganese dioxide either in acetone, in diluted sulphuric acid or in carbon tetrachloride. Secondary alcohols are oxidized to ketones more readily than primary ones, producing the best yields. This is because the secondary alcohols are more reactive than the primary ones, and the ketone obtained is more resistant than aldehyde to oxidizing agents. The ketones formed are removed by organic solvents from the reaction mixture, thus protecting them from further oxidation.

11.3. OXIDATION OF ALDEHYDES AND KETONES TO ACIDS

All the oxidizing agents which oxidize primary alcohols to aldehydes can also be used for obtaining, from aldehydes or alcohols, carboxylic acids with the same number of carbon atoms. But it is best to oxidize hydric primary alcohols to the corresponding acids without passing through the stage of aldehyde formation by using potassium permanganate in an alkaline medium, which has been created by the potassium hydroxide formed in the reaction:



When primary alcohols are oxidized by a chromic acid mixture and potassium permanganate in an acid medium, esters are formed as by-products.

In some cases, high yields are obtained by using nitric acid, which is employed mainly for obtaining carboxylic acids that are isolated from the reaction mixture in the form of sparingly water-soluble salts.

When secondary alcohols and ketones are being oxidized, an acid with the same number of carbon atoms cannot be obtained, because ketones are more resistant to oxidation than aldehydes.

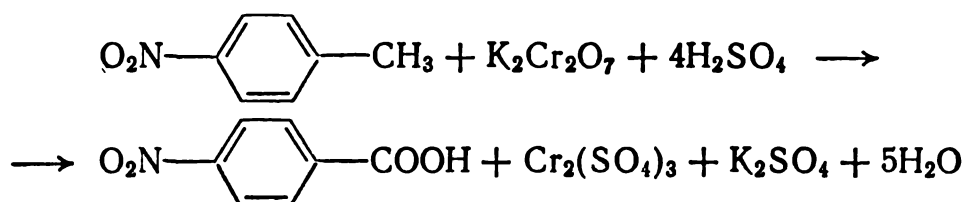
They are oxidized only with the rupture of the carbon chain, for which the oxidizing agents' action must be stronger and longer. Aliphatic ketones and secondary alcohols are oxidized either by a chromic acid mixture or by nitric acid with the formation of a mixture of fatty carboxylic acids.

The oxidation of alicyclic alcohols and ketones to dibasic carboxylic acids is of great practical importance. For instance, adipic acid is obtained by cyclohexanol oxidation.

11.4. OXIDATION OF METHYL AND METHYLENE GROUPS

Unbranched saturated hydrocarbons are the most sparingly oxidizable organic compounds. Oxidation begins only under drastic conditions, for instance, under the action of a hot chromic acid mixture. In this case, ketones, acids and other oxidation products are obtained. Therefore, the oxidation of saturated hydrocarbons is not a preparative method for obtaining definite compounds.

The methyl group is oxidized more readily if it is bonded with a double bond or an aromatic ring. The methyl groups at the benzene ring are oxidized by a chromic acid mixture, nitric acid or potassium permanganate to carboxyl groups. For instance, *p*-nitrobenzoic acid is obtained when *p*-nitrotoluene is oxidized:



The methylene and methyl groups adjacent to the carbonyl group or to the double and triple bonds can be oxidized by selenium dioxide SeO_2 .

11.5. PREPARATION OF QUINONES BY OXIDATION

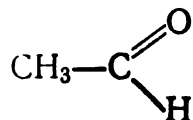
Certain aromatic compounds can be oxidized to *o*- and *p*-quinones by diverse oxidizing agents. For instance, hydroquinone is oxidized to *p*-benzoquinone under the action of sodium bichromate or sodium bromate in the presence of sulphuric acid.

Quinones are formed more readily from aromatic compounds when the double bonds in the α,β -positions to the carbonyl group in the compounds being obtained are united with the alkyl or aromatic groups. For instance, 2-methylnaphthalene is readily oxidized to 2-methyl-1,4-naphthoquinone, because the latter has methyl and aromatic groups in the α,β -positions to the carbonyl group.

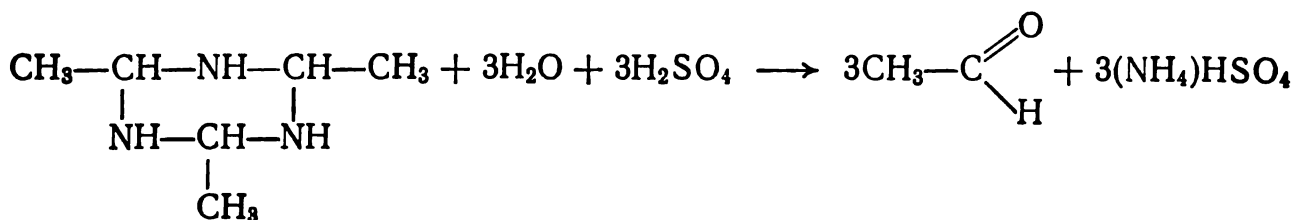
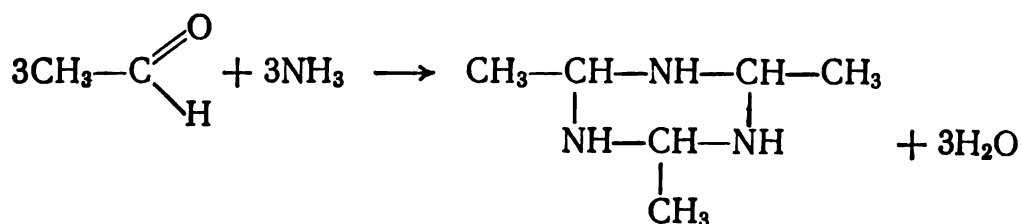
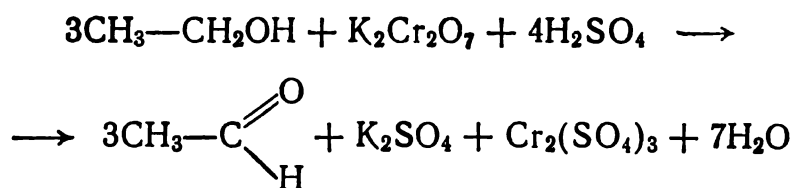
11.6. SYNTHESSES

ACETALDEHYDE

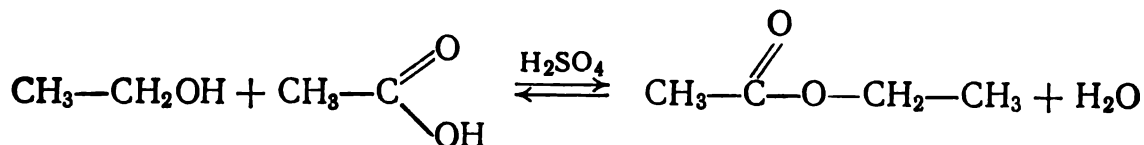
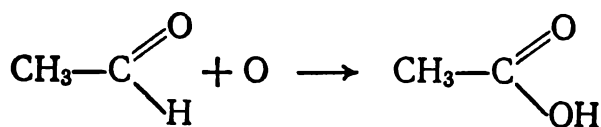
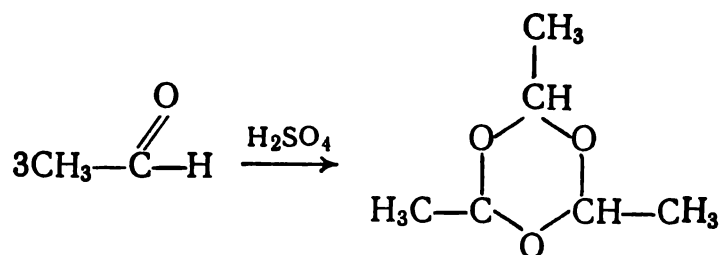
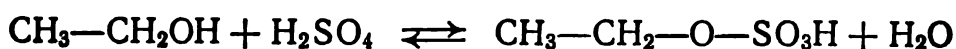
Formula:



Main reactions:



Side reactions:



Acetaldehyde irritates the mucous membranes and forms explosive mixtures with air!

Reagents and Equipment

Ethyl alcohol, 95 per cent	25 ml (0.4 mole)	Flasks, round-bottom, wide-mouth (250 and 500 ml)	2
Potassium dichromate	35 g (0.12 mole)	Condenser, Liebig	1
Sulphuric acid	35 ml	Condenser, coil	1
Ethyl ether	60 ml	Funnels, dropping	2
Carbon dioxide		Carbon dioxide cylinder or Kipp's generator	1
Cylinder ammonia		U-tube	1
Calcium chloride		Bottle, wash	1
Sodium chloride		Flask, Bunsen	1
Ice		Funnel, Büchner	1
		Thermometer (from -10°C to $+100^{\circ}\text{C}$)	1
		Flask, conical (300 ml)	1
		Beakers	5
		Flask, distilling	1

Assembly

1. A 500-ml round-bottom, wide-mouth flask is closed with a rubber stopper having three holes. A reflux condenser is inserted into one hole by means of a bent attachment, a dropping funnel with a long drawn-out tube is inserted into another, and a bent glass tube, which almost reaches the bottom of the flask, into the third one. The tube is used for connecting the apparatus to the carbon dioxide cylinder or the Kipp generator.

To overcome excess pressure, the upper tube of the Kipp generator is closed with a stopper through which a tube filled with dilute hydrochloric acid passes.

To equalize pressure, the upper opening of the dropping funnel is connected to a gas inlet tube. The upper end of the condenser is connected to a U-tube filled with calcined calcium chloride. The latter is connected through a coil condenser to a wash bottle containing 60 ml of ether.

If elevated pressure develops in the apparatus, preventing the inflow of the chromic acid mixture, pour the mixture in under carbon dioxide pressure. To this end, a T-piece is attached to the tube which supplies carbon dioxide, and the free end of the T-piece is connected by a rubber tubing with a screw clamp to the tube of the dropping funnel. The rate of chromic acid mixture supply is controlled by turning the screw clamp.

The wash bottle is immersed in a freshly prepared mixture of salt and ice (the temperature of the mixture should be no higher than -10°C). A thermometer, fastened by a thread to the stopper, is placed at the upper end of the condenser. The thermometer bulb should be in the middle of the inner tube of the condenser (Fig. 11.1).

2. Suction apparatus (see Fig. 2.21).

3. A 250-ml round-bottom, wide-mouth flask is placed in a water bath and tightly closed with a rubber stopper having four

holes. These holes have a dropping funnel, which almost reaches the bottom of the flask, a glass tube for introducing carbon dioxide, a wide tube, which connects the flask through a calcium chloride U-tube to the vertical coil condenser, and a thermometer. The condenser is connected by a glass tube to a receiver being cooled with a mixture of ice and salt (the receiver must be cooled, because acetaldehyde boils at 20.8°C).

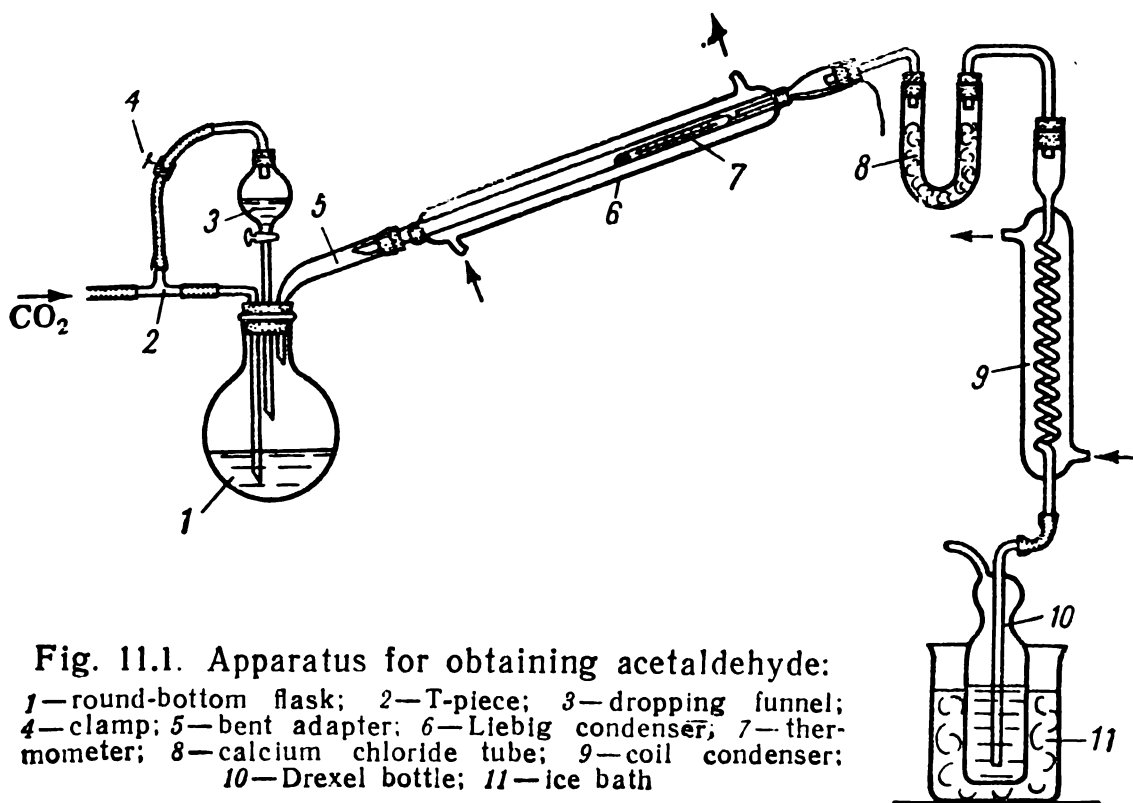


Fig. 11.1. Apparatus for obtaining acetaldehyde:

1—round-bottom flask; 2—T-piece; 3—dropping funnel; 4—clamp; 5—bent adapter; 6—Liebig condenser; 7—thermometer; 8—calcium chloride tube; 9—coil condenser; 10—Drexel bottle; 11—ice bath

Procedure

Work should be done *in a fume cupboard*. Twenty-five millilitres of ethyl alcohol and one-third of a mixture of 35 ml of concentrated sulphuric acid and 70 ml of water are poured into a round-bottom, wide-mouth flask (apparatus 1). The mixture is heated to boiling in a water bath. Another 35 ml of water are added to the remaining amount of dilute sulphuric acid and 35 g of potassium dichromate are dissolved in it (**caution: potassium dichromate is poisonous!**). Then the warm solution is poured into a dropping funnel; be sure that the entire funnel tube is filled with the liquid. Afterwards, a chromic acid mixture is added gradually to the boiling alcohol while so controlling the solution supply rate that the reaction mixture continuously boils and the thermometer in the condenser shows $25\text{--}30^{\circ}\text{C}$. Since the reaction is exothermic, the mixture continues to boil without being heated outside.

While adding the chromic acid mixture, a carbon dioxide stream is so passed through the liquid that the gas bubbles can be counted.

To prevent acetaldehyde from further oxidation, a weak carbon dioxide stream is passed through the reaction mixture. The stream carries away the acetaldehyde being formed together with a certain amount of the vapours of alcohol, water, acetal and ethylsulphuric acid.

In the condenser, a large part of acetaldehyde has time to condense, while acetaldehyde vapours which pass through the condenser are absorbed by the ether being cooled with a mixture of ice and salt.

In 20 min, the addition of the chromic acid mixture is stopped, but carbon dioxide is passed through for another 10 min to force acetaldehyde completely out of the flask. Afterwards, the wash bottle is disconnected from the apparatus, and only then is the supply of carbon dioxide stopped.

Acetaldehyde cannot be removed from ether by distillation, and therefore it should be converted into crystalline aldehyde ammonia. To this end, the contents of the wash bottle are poured into a beaker placed in a cooling mixture, and dry ammonia is supplied to a wide glass tube, which reaches the bottom of the flask, until the solution begins to smell strongly.

If there is no ammonia cylinder in the laboratory, ammonia is obtained by boiling a concentrated ammonia solution in a round-bottom flask fitted with a reflux condenser (a safety screen must be used for the burner). For drying, the ammonia being liberated is passed through a column filled with sodium hydroxide and soda lime into beaker 6 containing an ethereal acetaldehyde solution (Fig. 11.2).

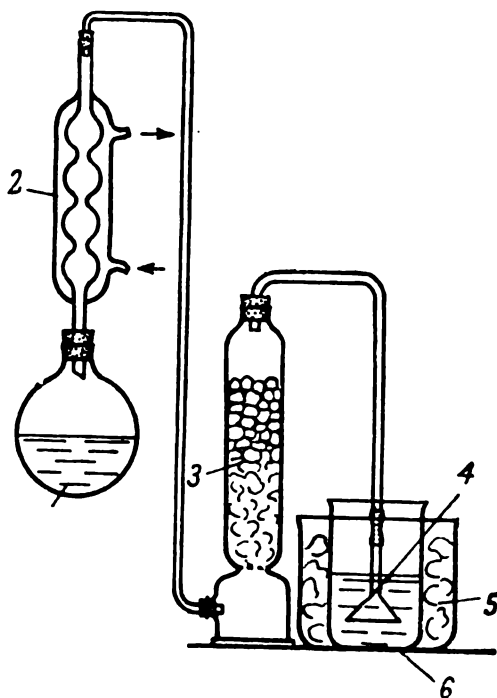


Fig. 11.2. Apparatus for obtaining ammonia:

1—round-bottom flask; 2—Allihn condenser; 3—absorption column with calcium chloride; 4—funnel; 5—ice bath; 6—beaker with an ethereal solution of acetaldehyde

The flask should be closed with a piece of cardboard that has an opening so that the reaction mixture can be stirred with a tube used for introducing ammonia, and so that the evaporation of ether can be reduced.

About six litres of ammonia are needed for completely binding aldehyde. The ethereal solution of acetaldehyde, saturated with ammonia, is allowed to stand for one hour in a cooling mixture. The mixture is sucked off in the Büchner funnel and the residue is washed with a small amount of ether and dried at first on filter paper and then in a desiccator over sulphuric acid. Pure aldehyde ammonia can be stored for a long time in a well closed bottle, while the contaminated preparation darkens and decomposes in

several days. The yield of crystalline aldehyde ammonia is about nine grams.

To obtain free acetaldehyde, apparatus 3 is assembled. The aldehyde ammonia obtained is put in a 250-ml round-bottom flask and 10 ml of water are poured in. A cooled mixture of 7 ml of concentrated sulphuric acid and 20 ml of water is put in a dropping funnel and added dropwise for 30 min, to the aldehyde ammonia solution.

The isolated acetaldehyde is distilled by heating the flask in a water bath. To prevent acetaldehyde from being oxidized, the apparatus is filled with carbon dioxide before distillation (carbon dioxide is not passed through during distillation because of the high pressure of acetaldehyde vapours; otherwise, a large amount of acetaldehyde will be lost).

At the end of distillation, carbon dioxide is again slowly passed through the apparatus for a short time. Acetaldehyde is collected in a receiver cooled by a mixture of ice and salt.

Acetaldehyde (acetic aldehyde) is a colourless liquid with suffocating pungent odour. It mixes well with water, alcohol, ether and chloroform. Its molecular weight is 44.05; b.p., 20.8 °C; m.p., -123.5 °C; d_4^{18} , 0.783; and n_D^{20} , 1.3316.

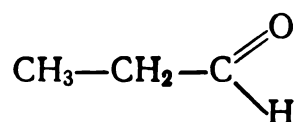
It is used for producing acetic acid, butadiene, acetaldol, and aldehyde synthetic resins. It is also employed in the laboratory and used for other purposes.

Characterization Tests. 1. A dark blue-violet colour appears when a 1 per cent aqueous solution of acetaldehyde is added to fuchsin sulphurous acid.

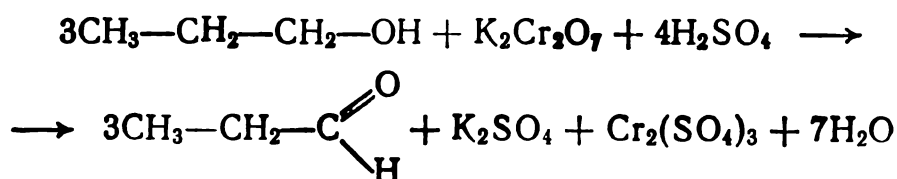
2. A dark red colour appears when 2 ml of a 0.5 per cent aqueous solution of sodium nitroprusside and two drops of a 10 per cent alkaline solution are added to 2 ml of an aqueous solution of acetaldehyde.

PROPIONALDEHYDE

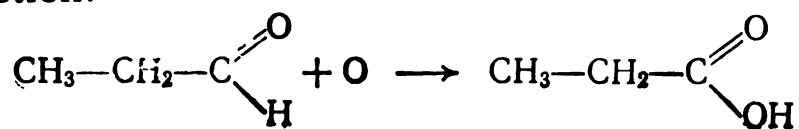
Formula:



Main reaction:



Side reaction:



Reagents and Equipment

Propyl alcohol	31 ml	Flask, round-bottom	1
	(0.4 mole)	Stirrer	1
Potassium dichromate	19 g	Funnel, dropping	1
	(0.06 mole)	Adapter, three-mouth	1
Sulphuric acid ($d = 1.84$)	36 ml	Condenser, Allihn	1
Sodium sulphate, anhydrous		Condenser, Liebig	1
		Adapter, bent	1
		Flask, Würtz (100 ml)	1
		Thermometer	1
		Receivers	2

Assembly

1. A three-mouth adapter, fitted with a stirrer, a dropping funnel and an Allihn reflux condenser, is inserted into a 500-ml round-bottom flask. Water heated to 60°C is passed through the Allihn condenser, which is secured at an angle of 45°.

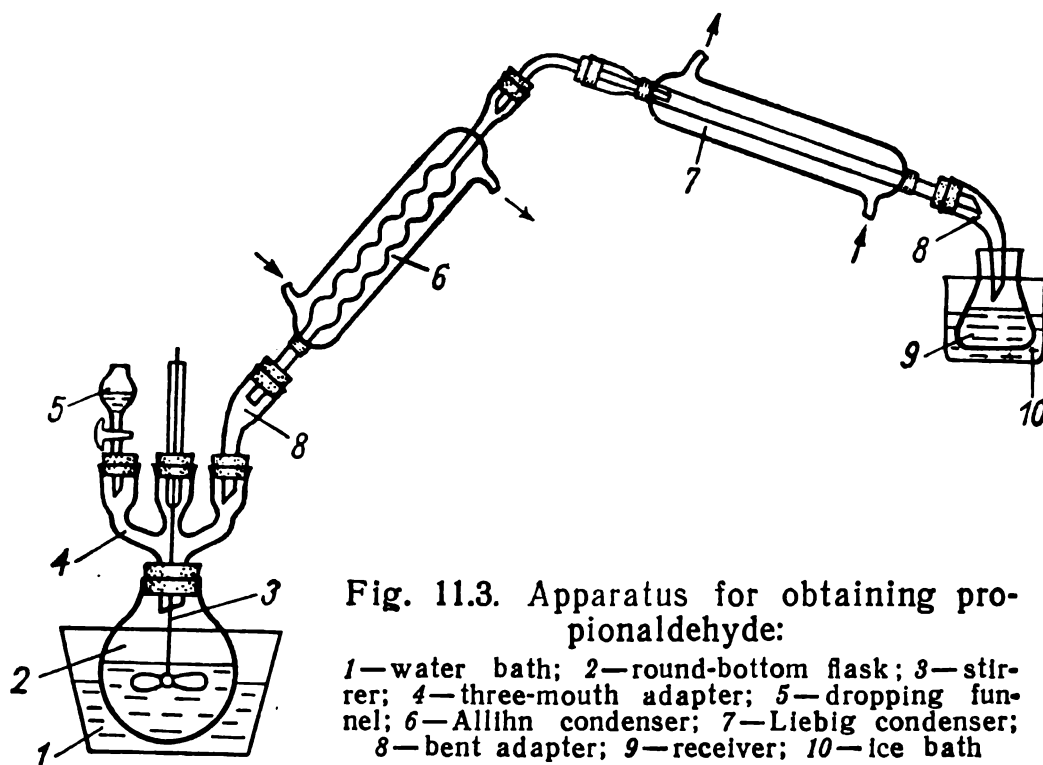


Fig. 11.3. Apparatus for obtaining propionaldehyde:

1—water bath; 2—round-bottom flask; 3—stirrer; 4—three-mouth adapter; 5—dropping funnel; 6—Allihn condenser; 7—Liebig condenser; 8—bent adapter; 9—receiver; 10—ice bath

A Liebig condenser through which cold water circulates is connected to the upper end of the Allihn condenser. The end of the second condenser is fitted with a bent adapter, which is put in a receiver being cooled with icy water.

The flask is placed in a water bath (Fig. 11.3).

2. A 100-ml Würtz distilling flask, placed in a water bath, is fitted with a thermometer and a Liebig condenser having a bent adapter, which is lowered into the receiver being cooled.

Procedure

Thirty-one millilitres of propyl alcohol are put in the round-bottom flask of apparatus 1 and heated until it boils. Afterwards, a chromic acid mixture of 19 g of potassium dichromate (see

p. 200), 36 ml of concentrated sulphuric acid and 300 ml of water is slowly added for 15-20 min through a dropping funnel. While the mixture is being added, the contents of the flask are stirred and intensely boiled. When all the chromic acid mixture has been put in, the contents of the flask are boiled for 15-20 min to drive off propionaldehyde traces. Aldehyde is then dried with anhydrous sodium sulphate. Dry propionaldehyde is distilled off at 50-55 °C in a water bath (apparatus 2). The propionaldehyde yield is about ten grams.

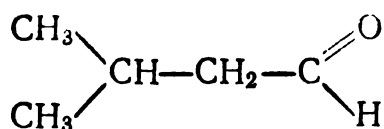
Propionaldehyde is a colourless liquid with a characteristic suffocating odour. It dissolves in water and mixes with alcohol and ether. Its molecular weight is 58.08; b.p., 48.8 °C; m. p., -81 °C; d_4^{20} , 0.8066; and n_D^{20} , 1.3635.

It is used as an intermediate in organic synthesis.

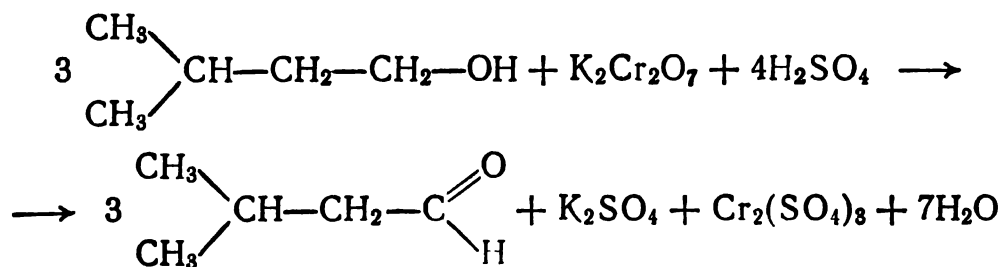
Characterization Test. A dark blue colour appears when 10 ml of a 1 per cent sodium nitroprusside solution and 0.5 g of piperazine are added to one drop of propionaldehyde.

ISOVALERALDEHYDE

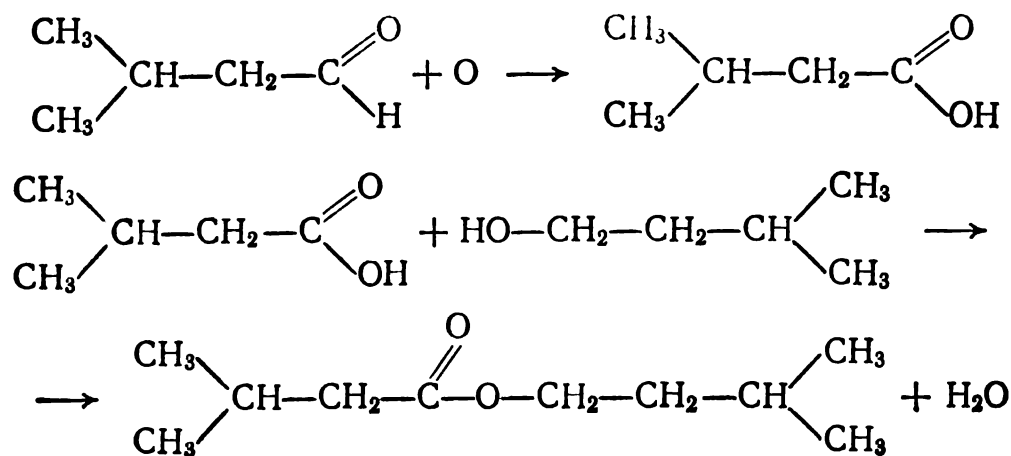
Formula:



Main reaction:



Side reactions:



Reagents and Equipment

Isoamyl alcohol	13.2 g (0.15 mole)	Flasks, Würtz (100 and 500 ml) . .	2
Potassium dichromate .	16.5 g (0.055 mole)	Funnel, dropping	1
Sulphuric acid ($d = 1.84$)	16 ml	Funnel, separatory	1
Sodium carbonate		Condenser, Liebig	1
Sodium bisulphite		Funnel, Büchner	1
Ether		Flask, Bunsen	1
Calcium chloride		Thermometer	1
		Adapter, bent	1
		Receivers	2

Assembly

1. A 500-ml Würtz distilling flask, placed in a water bath, is closed with a stopper having two holes. A dropping funnel is inserted in one hole, and a thermometer in the other. The side arm of the flask is connected to a Liebig condenser fitted with a bent adapter, whose end is lowered into a receiver.

2. Suction apparatus (see Fig. 2.21).

3. A 100-ml distilling flask is fitted with a thermometer and a Liebig condenser having a bent adapter, which is lowered into a receiver.

Procedure

A mixture of 16.5 g of potassium dichromate (see p. 200), 160 ml of water and 16 ml of concentrated sulphuric acid is put in the distilling flask of apparatus 1. The mixture is heated in a water bath to 90°C and isoamyl alcohol is carefully added dropwise from a dropping funnel while shaking the flask from time to time. Since alcohol oxidation is an exothermic reaction, the alcohol must be so added that the contents of the flask do not boil vigorously and eject. When the alcohol has been poured in, the flask is heated for another 15 min in a boiling water bath. In this case, isovaleraldehyde begins to be driven off.

Since isovaleraldehyde is poorly water-soluble, its further oxidation to isovaleric acid slows down. Therefore, there is no need to pass carbon dioxide through the reaction mixture.

The bath is removed, the flask is wiped outside and the mixture is heated with a burner over an asbestos gauze until it boils. In this case, isovaleraldehyde with impurities is driven off.

It is difficult to remove isovaleraldehyde from the reaction mixture because of its high boiling point (92.5°C). The reaction products will therefore have, besides aldehyde and a small amount of unreacted alcohol, isovaleric acid and its ester with isoamyl alcohol.

To remove acid traces, the distillate which separated into two layers is treated with sodium carbonate until litmus paper shows

an alkaline reaction. The upper layer, which consists of isovaleraldehyde and unreacted alcohol, is separated in a separatory funnel. Isovaleraldehyde is then shaken with an equal amount of a fresh saturated solution of sodium bisulphite. The precipitated crystals of derived isovaleraldehyde are sucked off in the Büchner funnel and washed with a small amount of ether, wrung between sheets of filter paper and dried over calcium chloride in a desiccator. The yield of derived isovaleraldehyde is about 15 g.

To isolate isovaleraldehyde, its derivative is treated with a sodium carbonate solution. Aldehyde is separated in a separatory funnel, dried with calcium chloride and distilled (apparatus 3).

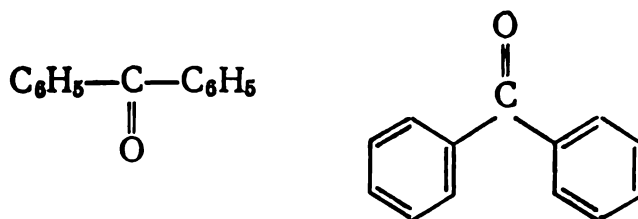
Isovaleraldehyde is a colourless liquid with an unpleasant odour. It dissolves sparingly in water and well in alcohol and ether. Its molecular weight is 86.14; b.p., 92.5 °C; m.p., -51 °C; d_4^{20} , 0.802; and n_D^{20} , 1.3902.

Characterization Tests. 1. Isovaleraldehyde with fuchsin sulphurous acid produces a violet colour.

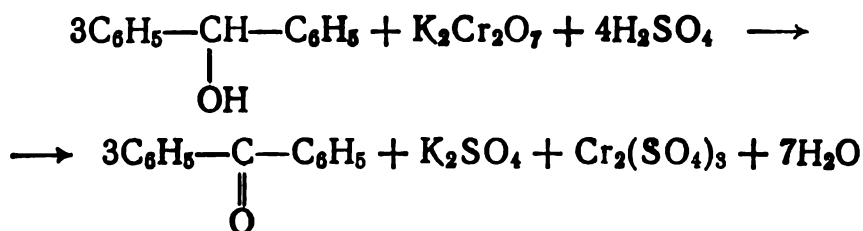
2. Orange-red needles of dinitrophenylhydrazone (m.p. 123 °C) will appear when a few drops of isovaleraldehyde are added to 5 ml of a 1-2 per cent solution of 2,4-dinitrophenylhydrazine in 95 per cent alcohol.

BENSOPHENONE

Formula:



Main reaction:



Reagents and Equipment

Benzhydrol	10 g (0.06 mole)	Flask, round-bottom, three-necked (200 ml)	1
Potassium dichromate	12 g (0.04 mole)	Flask, Würtz (100 ml)	1
Sulphuric acid ($d = 1.84$)	6 ml (0.1 mole)	Stirrer	1
		Condenser, Liebig	1
Benzene	75 ml	Thermometer	1
Potassium carbonate, anhydrous		Funnel, separatory	1
		Adapter, bent	1
		Flask, conical	1
		Beaker	1

Assembly

1. A 200-ml round-bottom, three-necked flask, fitted with a stirrer and a thermometer, is placed in a water bath.
2. A 100-ml Würtz flask, placed in a water bath, is connected to a thermometer and a Liebig condenser fitted with a bent adapter, whose end is lowered into a receiver (conical flask).
3. A small beaker is placed under the outlet tube of a 100-ml Würtz distilling flask.

Procedure

A chromic acid mixture is prepared in the round-bottom three-necked flask of apparatus 1 by successively putting 12 g of potassium dichromate (see p. 200), 60 ml of water and 6 ml of concentrated sulphuric acid in the flask. The mixture is heated to 40 °C in a water bath and 10 g of benzhydrol are added in portions through an opening while stirring the mixture. When all the benzhydrol has been added to the reaction mixture, the contents of the flask are stirred for one hour at 40-50 °C (in this synthesis, the temperature conditions should be strictly maintained).

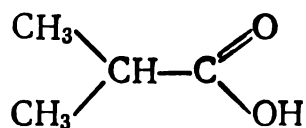
Apparatus 2 is assembled and benzene is driven off at 80-90 °C. The benzophenone which remains in the Würtz flask is distilled without a condenser after putting a beaker under the end of the outlet tube of the flask.

The benzophenone yield is about nine grams. The properties of benzophenone are given on page 193.

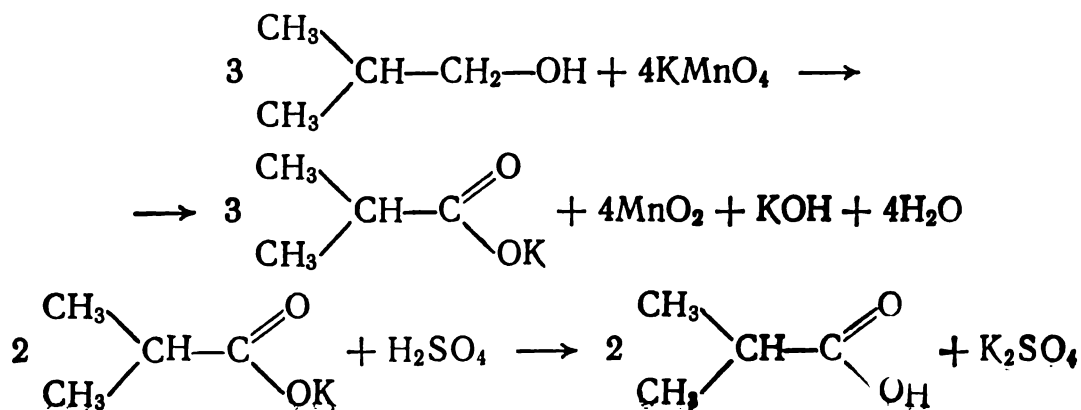
Characterization Test. Benzophenone dissolves in concentrated sulphuric acid, producing a yellow colour.

ISOBUTYRIC ACID

Formula:



Main reactions:



Reagents and Equipment

Isobutyl alcohol	14.8 g or 18 ml (0.2 mole)	Flasks, round-bottom (1000 ml)	3
Potassium permanganate	42 g (0.27 mole)	Flask, Würtz (100 ml)	1
Sodium carbonate	12 g	Flask, Bunsen	1
Ethyl ether	50 ml	Funnel, Büchner	1
Sulphuric acid, 50 per cent		Funnel, separatory	1
Magnesium sulphate, anhydrous		Condenser, Liebig	1
		Condenser, air	1
		Adapter, bent	1
		Thermometer	1
		Beaker	1
		Receivers	2

Assembly

1. A 1000-ml round-bottom flask is placed in a water-and-ice bath.
2. Suction apparatus (see Fig. 2.21).
3. A 100-ml Würtz distilling flask is placed in a water bath and connected to a thermometer and a Liebig condenser fitted with a bent adapter, which is lowered into a receiver.
4. A Würtz distilling flask fitted with a thermometer is connected to an air condenser and heated by a small burner flame.

Procedure

Eighteen millilitres of isobutyl alcohol, 45 ml of water and 12 g of sodium carbonate are put in the round-bottom flask of apparatus 1 (isobutyric acid is obtained in an alkaline medium, because less by-products are formed in it). The mixture formed is cooled and a preliminarily cooled solution of 42 g of potassium permanganate and 800 ml of water is gradually added in small portions while continuously stirring the mixture. In this case, the flask is cooled; the temperature of the reaction mixture must be 12-15 °C. After potassium permanganate is poured in, the reaction mixture is cooled to 2 °C and allowed to stand for 10-12 hours at room temperature.

The decolorization of the potassium permanganate solution indicates the end of the oxidation reaction. If the solution has not decolorized, stirring should be continued until the crimson colour disappears. If the mixture is still coloured, a small amount of ethyl alcohol or oxalic acid is added.

The manganese dioxide precipitate is sucked off in the Büchner funnel and the filtrate is boiled down to 40 ml in a water bath. The boiled-down solution is cooled and poured into a separatory funnel, and 50 per cent sulphuric acid is introduced until congo red shows an acid reaction, and then 20 ml of ether are added. The contents of the separatory funnel are shaken and allowed to separate into

layers, and then the water layer is separated and treated twice with ether (10 ml every time). The combined ethereal extracts are dried with anhydrous manganese sulphate.

Anhydrous manganese sulphate is a good neutral drying agent for many organic compounds. It may be replaced by anhydrous sodium sulphate, which is a cheaper drying agent, but it lacks rapidity and intensity.

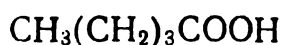
After drying, apparatus 3 is assembled, ether is driven off in a water bath, the residue is distilled (apparatus 4), and the fraction which boils at 150-158 °C is collected. The isobutyric acid yield is about 14 g.

Isobutyric acid is a colourless liquid with a rancid oil odour. It dissolves in water (20 g in 100 ml of water at 20 °C) and mixes with alcohol, ether and chloroform. Its molecular weight is 88.10; b.p., 154.7 °C; m. p., -46.1 °C; d_4^{15} , 0.9527; and n_D^{20} , 1.3930.

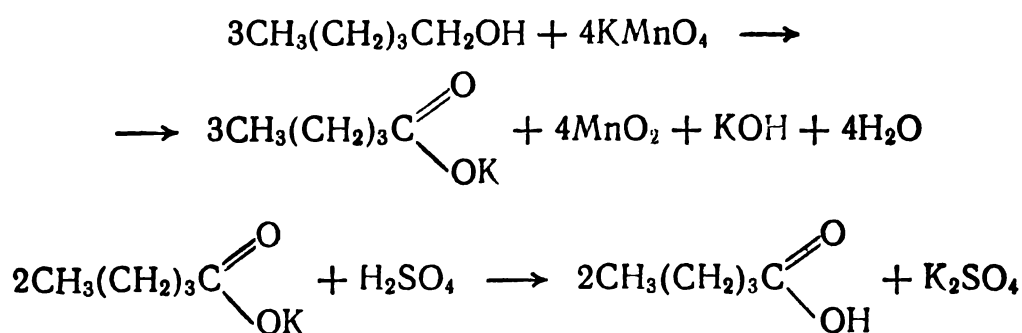
Characterization Test. An equal amount of acetone is added to a solution of calcium salt of isobutyric acid saturated in the cold. Needle crystals precipitate in one hour.

VALERIC ACID*

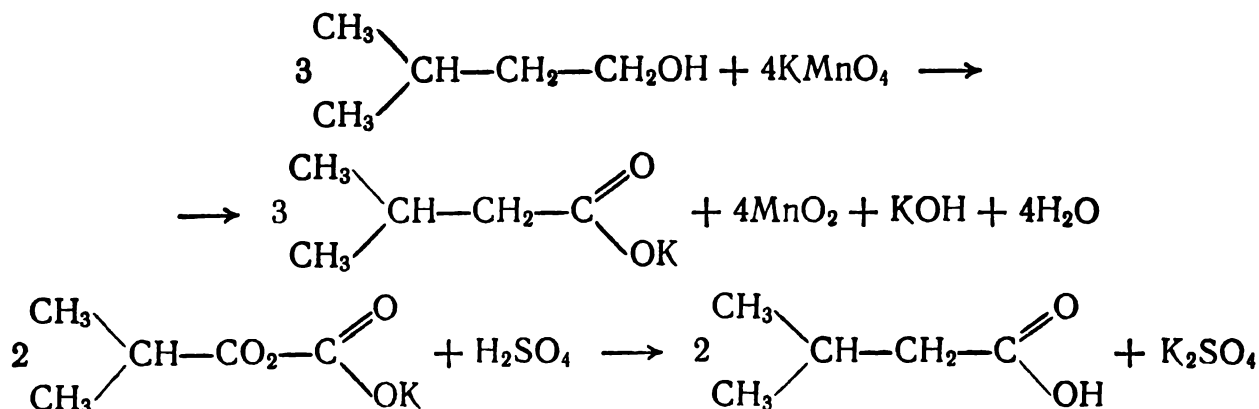
Formula:



Main reactions:



* Isovaleric acid is obtained similarly from isoamyl alcohol.



The reagents used in this case are: isoamyl alcohol (22 ml), potassium permanganate (42 g), sodium hydroxide, sodium sulphate, 50 per cent sulphuric acid, carbon tetrachloride, and ice. The isovaleric acid yield is about 16 g.

Reagents and Equipment

Amyl alcohol	10 g or 12 ml (0.11 mole)	Flask, round-bottom, wide-mouth (500 ml)	1
Potassium permanganate	24 g (0.14 mole)	Flask, Würtz (100 ml)	1
Sodium hydroxide	4.3 g	Adapter, three-mouth	1
Sodium sulphate, anhydrous	4 g	Stirrer	1
Sulphuric acid, 50 per cent	18 ml	Funnel, dropping	1
Carbon tetrachloride . .	12 g	Flask, Bunsen	1
Ice		Funnel, Büchner	1
		Condenser, Liebig	1
		Condenser, air	1
		Adapter, bent	1
		Thermometer	1
		Receivers	3

Assembly

1. A 500-ml round-bottom, wide-mouth flask is closed with a stopper having a three-mouth adapter, which is fitted with a stirrer and a dropping funnel.

2. Suction apparatus (see Fig. 2.21).

3. A thermometer is inserted in the neck of the 100-ml distilling flask, while the side arm of the flask is connected to a Liebig condenser fitted with a bent adapter, whose end is lowered into a receiver. The flask is placed in a water bath.

4. A 100-ml distilling flask is connected to a thermometer and an air condenser.

Procedure

Twenty-four grams potassium permanganate, 10 ml of water and 4.3 g of sodium hydroxide are put in the round-bottom, wide-mouth flask of apparatus 1. The contents of the flask are stirred well and 12 ml of amyl alcohol are slowly added from a dropping funnel for one hour while simultaneously adding 160 g of crushed ice to the reaction mixture. In this case, the temperature of the reaction mixture should be maintained at 18-24 °C. After amyl alcohol is put in, the mixture is stirred for another 30 min and allowed to stand for 10-12 hours at room temperature.

The manganese dioxide precipitate is sucked off in the Büchner funnel. The filtrate is boiled down to 30 ml in a water bath and cooled, and then, in order to separate valeric acid from its potassium salt, 18 ml of 50 per cent sulphuric acid are added until congo red shows an acid reaction.

The liquid is transferred to a separatory funnel and the valeric-acid layer formed is separated. Acid residues in the water layer are extracted three times with carbon tetrachloride (caution: carbon tetrachloride cannot be dried with metallic sodium, because

there may be an *explosion*; carbon tetrachloride *irritates the mucous membranes and causes headaches*).

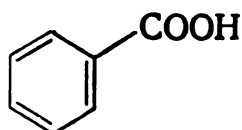
The combined extracts are added to the main portion of valeric acid and dried over four grams of anhydrous sodium sulphate. Carbon tetrachloride is then driven off at 80 °C (apparatus 3), the residue is distilled (apparatus 4), and valeric acid is collected at 184-187 °C. The valeric acid yield is about eight grams.

Valeric acid is a colourless liquid with a characteristic unpleasant odour. It dissolves sparingly in water and well in alcohol, ether and carbon tetrachloride. Its molecular weight is 102.14; b.p., 186.4 °C; m.p., -35 °C; *d*, 0.939, and n_D^{20} , 1.4086.

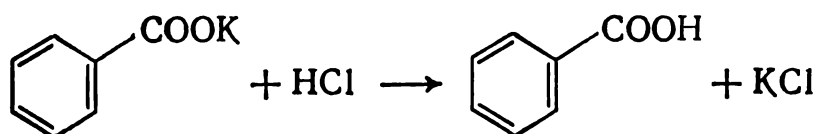
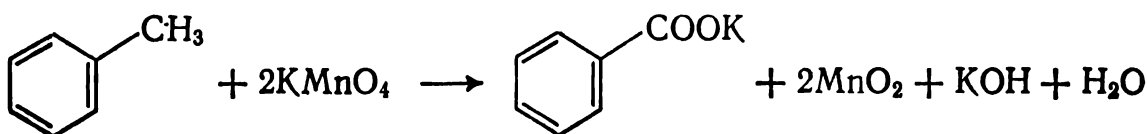
It is used in the food industry and in making perfume, as well as for producing synthetic articles.

BENZOIC ACID

Formula:



Main reactions:



Toluene is oxidized in an alkaline medium, which is created by the potassium hydroxide formed in the reaction.

Reagents and Equipment

Toluene	2g or 2.5 ml (0.02 mole)	Flask, round-bottom (150 ml) . . .	1
Potassium permanganate	3.2 g (0.02 mole)	Condenser, Liebig	1
		Stirrer	1
		Head, still	1
Hydrochloric acid		Thermometer	1
		Adapter, bent	1
		Funnel, Büchner	1
		Flask, Bunsen	1
		Receiver	1

Assembly

1. A 150-ml round-bottom flask, placed in a sand or water bath, is fitted with a still head having a reflux condenser and a stirrer.
2. Suction apparatus (see Fig. 2.21).

Procedure

Put 2.5 ml of toluene (**caution:** the inhalation of toluene vapours affects the nervous system!), 3.2 g of finely ground potassium permanganate and 75 ml of water in the round-bottom flask of apparatus 1. The contents of the flask are heated in a boiling water bath (or a sand bath) for three hours while stirring the solution until it has decolorized. If the solution remains pink after heating, some oxalic acid or several drops of alcohol are added (these additives completely reduce potassium permanganate and the solution is decolorized).

After the reaction is completed and the mixture is cooled, the manganese dioxide precipitate is filtered off in a small Büchner funnel and washed twice with a small amount of hot water. The combined filtrate is boiled down to 15-20 ml in a water bath (or in a dish on a sand bath*). The manganese dioxide precipitate is filtered off again and washed once with 5 ml of hot water. The filtrate, i.e., a potassium benzoate solution, is converted into free benzoic acid under the action of dilute (1 : 1) hydrochloric acid (which is added until congo red shows a clearly acid reaction).

The benzoic acid precipitate is sucked off in a small Büchner funnel, washed with some cold water and dried. The benzoic acid yield is about two grams.

Benzoic acid is a colourless crystalline substance which dissolves sparingly in cold water (0.2 g in 100 ml of water at 18 °C and 2.2 g at 75 °C) and well in chloroform, acetone, carbon tetrachloride, benzene and methyl alcohol. Its molecular weight is 122.12; b.p., 250 °C, and m.p., 122.3 °C.

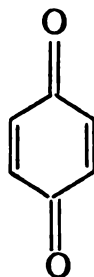
Benzoic acid and its derivatives are employed in the food industry and in making perfume, and are used for producing dyes and pharmaceuticals and for other purposes.

Characterization Test. A drop of a 0.3 per cent hydrogen peroxide solution and the same amount of a 1-3 per cent ferric chloride solution are added to 1 ml of an aqueous benzoic acid solution. A red-violet colour will quickly appear when the test tube is put in boiling water (oxidation produces salicylic acid which reacts with ferric chloride, giving this colour).

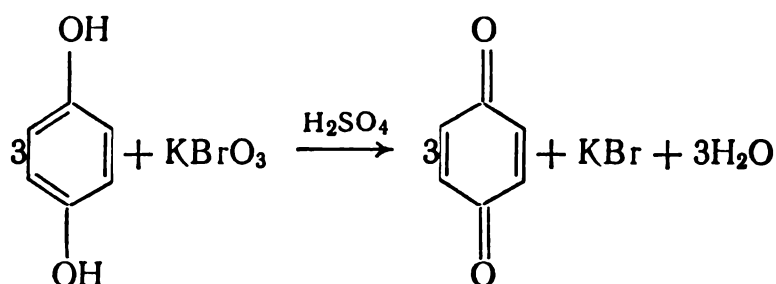
* When the amount of the initial products used is larger than in the foregoing example, unreacted toluene should be driven off from the same flask after the reaction, replacing the reflux condenser with a downflow one.

BENZOQUINONE

Formula:



Main reaction:



p-Benzoquinone is a *poison* which irritates the *mucous membranes* and leaves brown spots on the skin.

Reagents and Equipment

Hydroquinone	10 g (0.09 mole)	Flask, round-bottom (200 ml) . . .	1
Potassium bromate . . .	5.5 g (0.03 mole)	Thermometer	1
Sulphuric acid, 5 <i>N</i> solution	5 ml	Flask, Bunsen	1
		Funnel, Büchner	1

Assembly

1. A 200-ml round-bottom flask is placed in a water bath and fitted with a thermometer which is secured in a stand claw.
2. Suction apparatus (see Fig. 2.21).

Procedure

Ten grams of hydroquinone and 100 ml of water heated to 50°C are put in the round-bottom flask of apparatus 1. When hydroquinone dissolves, the solution is cooled to 20°C, and then 5 ml of sulphuric acid, which act as a catalyst, are slowly added in small portions.

When the hydroquinone used is not quite pure, a black sticky precipitate is formed as soon as sulphuric acid is added. To get rid of this precipitate, the liquid is passed through a fluted filter before adding the oxidizing agent, which in this case is potassium bromate.

Potassium bromate in an amount of 5.5 g is carefully added to the reaction mixture while heating the flask to 60°C in a water

bath. A reaction immediately begins with the formation of a greenish black precipitate, which is quinhydrone.

The oxidation of hydroquinone to *p*-benzoquinone gives an intermediate consisting of a hydroquinone molecule and a *p*-benzoquinone molecule, known as quinhydrone, whose colour intensification is due to the simultaneous presence of the quinoid and benzene rings in the molecule.

Heating is now stopped, because the temperature rises spontaneously to 75°C. The oxidation reaction is considered to be complete as soon as the black colour of the reaction mass changes to the bright yellow colour of benzoquinone. The reaction mixture is heated at 80°C until benzoquinone completely dissolves, and then it is cooled to 0°C. The *p*-benzoquinone precipitate is filtered off in the Büchner funnel, washed with a small amount of icy water and dried. The yield of *p*-benzoquinone (m.p. 116°C) is about eight grams.

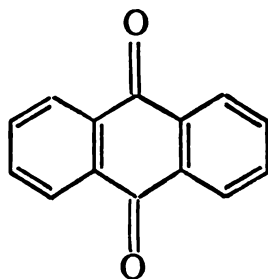
p-Benzoquinone is a gold-yellow crystalline substance with a characteristic odour. It dissolves sparingly in water in the cold and well in hot water, alcohol, ether and benzene. Its molecular weight is 108.09; m.p., 115.7°C, and d_4^{20} , 1.318. *p*-Benzoquinone is stored in dark bottles having ground-glass stoppers.

It is used for obtaining hydroquinone and is employed as oxidizing and tanning agents.

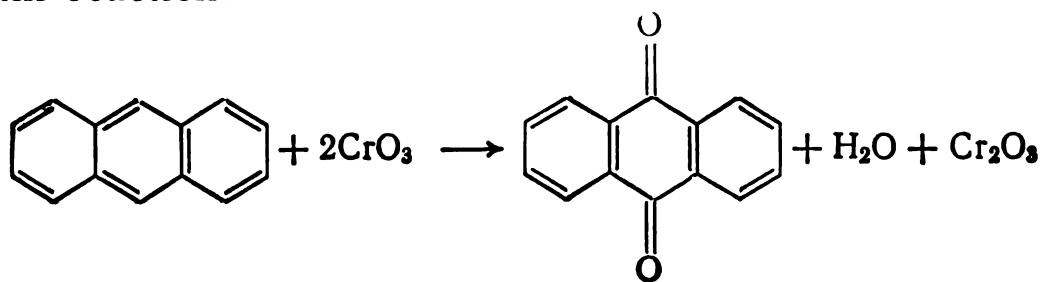
Characterization Test. Two test tubes are taken and 3 ml of ligroin are poured into each of them. Afterwards, some *p*-benzoquinone is dissolved in one test tube and the same amount of phenol in the other. When both solutions are mixed and cooled, red phenoquinone needles fall out.

ANTHRAQUINONE

Formula:



Main reaction:



Anthracene is very readily oxidized to anthraquinone under the action of various oxidizing agents (chromic anhydride in acetic acid, potassium permanganate, etc.). Even nitric acid acts as an oxidizing agent, and not as a nitrating agent, on anthracene.

Reagents and Equipment

Anthracene	2.5 g (0.014 mole)	Flask, round-bottom (300 ml) . . .	1
Acetic acid, glacial . . .	150 ml (2.5 mole)	Condenser, reflux	1
Chromic anhydride . . .	10 g (0.1 mole)	Funnel, dropping	1
Sodium hydroxide		Head, still	1
		Beaker	1
		Funnel, Büchner	1
		Flask, Bunsen	1

Assembly

1. A 300-ml round-bottom flask is fitted with a still head having a reflux condenser and a dropping funnel.
2. Suction apparatus (see Fig. 2.21).

Procedure

A solution of 10 g of chromic anhydride in 10 ml of water, as well as 40 ml of glacial acetic acid, are added from a dropping funnel to 2.5 g of finely ground anthracene in 110 ml of glacial acetic acid (**caution: anthracene irritates the mucous membranes**) in the round-bottom flask of apparatus 1 for one hour while boiling the contents of the flask. When all the chromic anhydride has been added (the green colour of the reaction mixture indicates that the reaction is complete), the mixture is then transferred to a beaker, where it is cooled and diluted with 300 ml of water. Afterwards, the mixture is allowed to stand for one hour; then, the anthraquinone crystals which precipitate are sucked off and washed with water diluted with an alkaline solution to neutralize acetic acid, and again with water and dried. The anthraquinone yield is about two grams.

If pure anthracene is used for oxidation, anthraquinone is purified by sublimation, and if commercial anthracene is used, anthraquinone is heated to 100°C with a five-fold (according to mass) amount of 10 per cent sulphuric acid for 10 min, and the mixture is then allowed to stand in a damp place for 12 hours. After pouring the mixture into water, the crystals of pure anthraquinone which have precipitated are filtered off, washed with a sodium carbonate solution and water, and dried.

Anthraquinone is a light yellow crystalline substance. It dissolves sparingly in water, alcohol and ether, and well in concentrated sulphuric acid, a hot sodium acetate solution, aniline, nitrobenzene and hot toluene. Its molecular weight is 208.20; b.p., 378-381 °C; m.p., 285-286 °C, and *d*, 1.438.

It is used for producing vat dyes and lacquers, and for other purposes.

Characterization Test. A few small crystals of anthraquinone and 2-3 ml of a dilute alkaline solution are put in a test tube. The mixture is heated until it boils, some zinc dust is added, and then it is heated for another 1-2 min and cooled. A bright red colour appears when hydrogen bubbles are no longer formed, and the solution decolorizes when shaken.

Chapter 12

NITRATION REACTIONS

Nitration is the introduction of a nitro group into the molecule of an organic compound. The nitration of aromatic compounds usually occurs readily and is one of the most important reactions in organic chemistry.

Nitro compounds of the aromatic series are intermediates in the production of dyes and medicinals, and are used also in making perfume. Many nitro compounds of the aromatic series, e.g., trinitrotoluene, trinitrobenzene and picric acid, are used as explosives.

Nitro compounds of the fatty series are used as solvents of synthetic resins, lubricants, dyes and nitrocellulose and as intermediates in numerous syntheses, e.g., syntheses of carboxylic acids, hydroxylamine, oximes, nitroalcohols, nitroolefins, etc.

A nitro group is introduced into the molecule of an organic compound by means of various nitrating agents.

The main nitrating agents are:

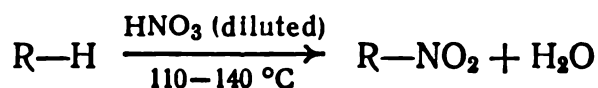
- (1) nitric acid of various concentrations;
- (2) nitrating mixture (a mixture of concentrated nitric and sulphuric acids);
- (3) nitrates of alkaline metals in the presence of sulphuric acid;
- (4) nitrogen oxides;
- (5) nitrates of metals in the presence of acetic anhydride and acetic acid;
- (6) a mixture of nitric and sulphuric acids with glacial acetic acid or acetic anhydride;
- (7) acetyl nitrate and benzoyl nitrate;
- (8) nitrates.

12.1. NITRATION OF HYDROCARBONS OF THE FATTY SERIES

Hydrocarbons of the fatty series do not react with concentrated nitric acid at room temperature. On heating, concentrated nitric acid oxidizes them. In this case, the carbon chain is ruptured with the formation of carboxylic acids.

To nitrate hydrocarbons of the fatty series, use dilute nitric acid, which does not produce a nitrating effect, but serves only as

a source of nitrogen dioxide, which is the real nitrating agent. Nitration occurs by the following scheme:

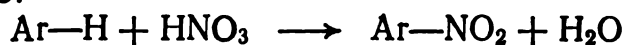


This reaction is called Konovalov's reaction, because M. I. Konovalov discovered and studied it in detail in the 1890's.

For preparative purposes, use is usually made of the action of silver nitrite on the halogen derivatives of the fatty series. An insignificant amount of a by-product (nitrite) will be formed, but it is easily separated.

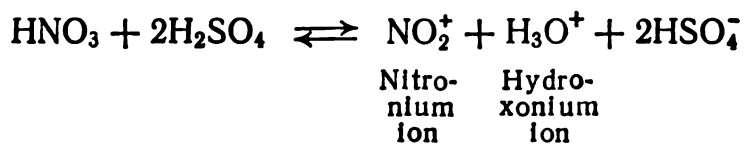
12.2. NITRATION OF HYDROCARBONS OF THE AROMATIC SERIES

Aromatic compounds are characterized by their ability to be converted into nitro compounds when they interact with nitric acid. The nitration of an aromatic compound can be represented by the following scheme:



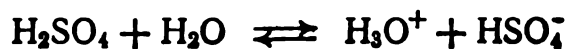
The reaction scheme given above shows that the nitration of aromatic compounds by nitric acid involves the formation of water, i.e., a decrease in the concentration of nitric acid. Dilute nitric acid is a strong oxidizing agent, resulting in the formation of by-products. To avoid this, a nitrating mixture (a mixture of concentrated nitric and sulphuric acids) is usually used for nitration.

Sulphuric acid promotes the formation of the nitronium ion (NO_2^+), which is the real nitrating agent in the nitration of the aromatic ring:

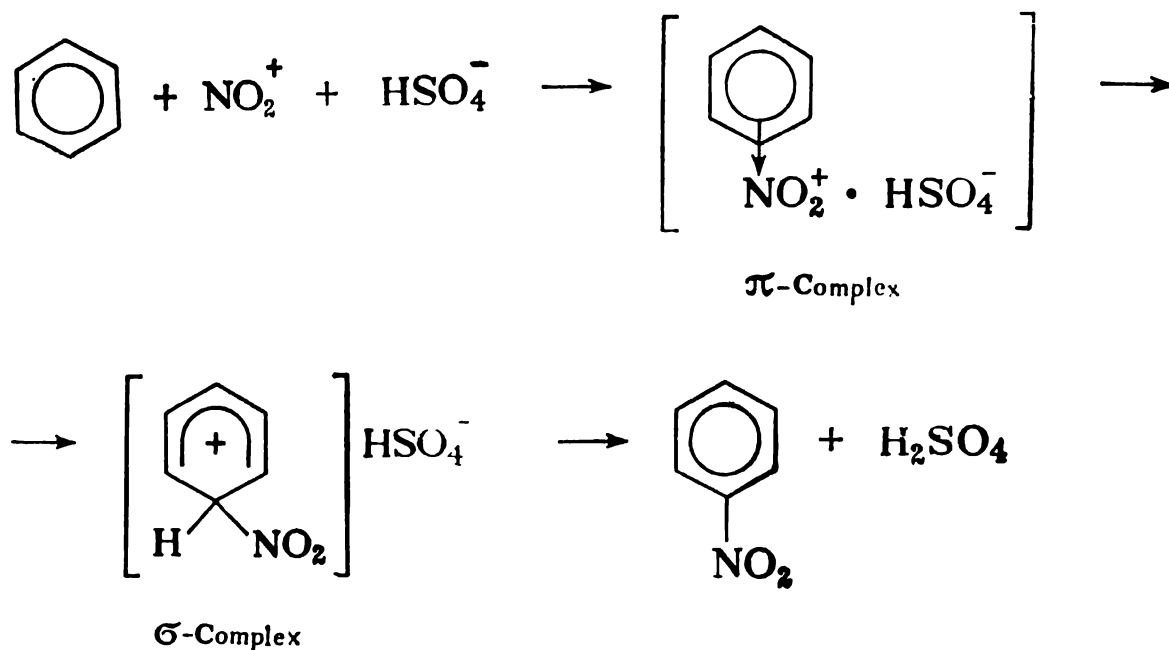


A study of the spectrum of the HNO_3 solution in strong acids shows that the nitronium ion exists in a large concentration. The fact that the nitronium ion really participates in nitration by a nitrating mixture has been proven by measuring the reaction rate.

When the nitrating mixture is diluted with water, the concentration of nitronium ions diminishes owing to the dissociation of sulphuric acid accompanying the formation of hydroxonium and bisulphate ions:



The nitronium ion interacts with aromatic hydrocarbon, as a result of which a nitro compound is formed:



It has been ascertained that the best yields of nitration products are obtained when 90 per cent sulphuric acid is employed. To estimate the site where a nitro group enters the aromatic ring, use the approximation orientation rules:

(1) substituents of the first kind ($-\text{OH}$, $-\text{NH}_2$, $-\text{NHR}$, $-\text{N}=\text{N}-$, $-\text{CH}_2\text{Cl}$, $-\text{CH}_2\text{R}$, $-\text{CH}_3$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$) orient the nitro group mainly in the *ortho*- and *para*-positions, and facilitate (besides halogens) its introduction into the ring;

(2) substituents of the second kind ($-\text{SO}_3\text{H}$, $-\text{NO}_2$, $-\text{COOH}$, $-\text{COOR}$, $-\text{CN}$, $-\text{CCl}_3$, $-\text{NH}_3^+$, $-\text{NH}_2\text{R}^+$) orient the nitro group mainly in the *meta*-position and hinder its introduction into the ring.

For instance, when the second nitro group is introduced into the aromatic ring, it is oriented in the *meta*-position to the nitro group which is already present. When introducing the second nitro group into the aromatic ring, the conditions must be more severe, i.e., the temperature and the acid concentration must be higher.

Phenol and toluene are nitrated far more readily than benzene because they contain *ortho*-, *para*-directing substituents ($-\text{OH}$, $-\text{CH}_3$), which make it easier for a nitro group to enter the ring. For instance, toluene is nitrated at 20-30 °C, while phenol can be nitrated with dilute nitric acid at 0-20 °C. The nature of the substituents in the benzene ring affects not only the nitration conditions and the site of entry of the second substituent, but also the reaction rate. The substituents $-\text{CH}_3$, $-\text{OCH}_3$, $-\text{OC}_2\text{H}_5$ and $-\text{OH}$ (the groups are arranged in the order of their growing directive power) accelerate nitration, while the substituents $-\text{COOH}$, $-\text{SO}_3\text{H}$ and

—NO₂ retard it. For instance, toluene is nitrated 24 times faster than benzene (owing to the presence of the —CH₃ substituent), while nitrobenzene is nitrated 10⁵ times slower (owing to the presence of the —NO₂ substituent).

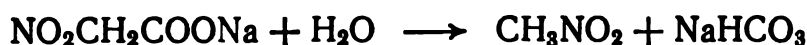
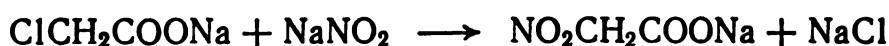
12.3. SYNTHESSES

NITROMETHANE

Formula:



Main reactions:



Side reaction:



Nitromethane is very *poisonous*!

Reagents and Equipment

Monochloroacetic acid .	18.9 g	Flasks, distilling (50 and 200 ml)	2
	(0.2 mole)	Condenser, Liebig	1
Sodium nitrite	14 g	Flask, conical	1
	(0.2 mole)	Funnel, separatory	1
Sodium carbonate	11 g	Thermometer	1
Calcium chloride		Adapter, bent	1
		Receiver	1

Assembly

A 200-ml reaction flask is connected to a thermometer, whose bulb should be in the liquid, and to a Liebig condenser which operates well and is fitted with a bent adapter. The receiver is a conical flask cooled with water.

Procedure

Monochloroacetic acid (**caution: it causes skin burns!**) in an amount of 18.9 g and 50 ml of cold water are put in the 200-ml reaction flask. The mixture is gradually neutralized with 11 g of sodium carbonate while thoroughly stirring it with a glass spatula until an alkaline reaction occurs (phenolphthalein test). In neutralization, the temperature should be no higher than 20 °C. Afterwards, a solution of 14 g of sodium nitrite in 40 ml of water is added to the reaction flask, the apparatus is assembled and the flask is heated by a small flame over a gauze.

The burner is removed as soon as carbon dioxide begins to bubble at 80-85°C. At this temperature, the reaction continues without external heating, and the nitromethane formed is driven off with water in heavy oily drops.

Nitromethane begins to be driven off at about 90°C. In this case, 15 ml of water are separated per 5 ml of nitromethane.

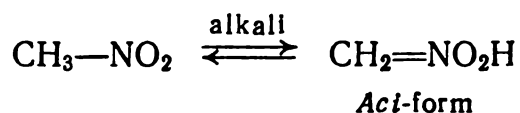
In the course of distillation, the contents of the flask become brown and the temperature rises to 100°C. When the reaction is fairly well completed, the reaction mixture is carefully heated to 110°C for 10 min. Distillation is stopped when water without oil begins to pass into the receiver. The distillate obtained is transferred to a separatory funnel and the lower nitromethane layer is separated from the upper water layer.

Nitromethane is dried with calcium chloride and distilled from a small distilling flask at 98-102°C. The nitromethane yield is about four grams.

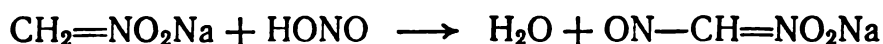
Pure nitromethane is a colourless liquid with a peculiar odour similar to that of bitter almond. Its molecular weight is 61.042; b.p., 102°C at 760 mm Hg; m.p., -29.0°C; d_4^{20} , 1.13816; and n_D^{20} 1.38188.

It is used as a solvent, e.g., for cellulosic compounds and vinyl resins, and as fuel for rockets and as an additive to diesel fuel.

Characterization Test. A few drops of nitromethane are mixed with 1 ml of water and 2-3 drops of a concentrated alkaline solution. The liquid formed is cooled with cold water. Afterwards, 1 ml of a sodium nitrite solution is poured in and dilute sulphuric acid is added dropwise until the red solution becomes yellowish. Alkali is then added again until a bright red colour appears. These reactions are caused by the tautomerism of the nitro compounds of the fatty series:



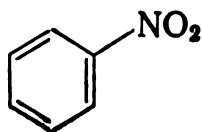
An alkaline medium engenders the salt $\text{CH}_2\text{=NO}_2\text{Na}$, which can react with HNO_2 ($\text{NaNO}_2 + \text{H}_2\text{SO}_4$):



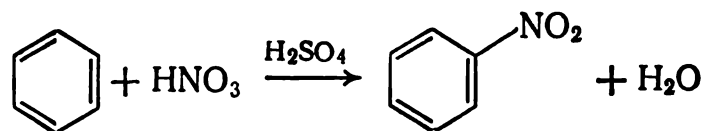
Primary and secondary nitro compounds react with nitrous acid, while the tertiary ones do not.

NITROBENZENE

Formula:



Main reaction (see p. 219):



Reagents and Equipment

Benzene	15.6 g or 18 ml (0.2 mole)	Flask, round-bottom (250 ml)	1
Nitric acid ($d = 1.4$) . . .	28 g or 20 ml (0.28 mole)	Flask, conical (50 ml)	1
Sulphuric acid ($d = 1.84$) .	46 g or 25 ml (0.45 mole)	Flask, Würtz (100 ml)	1
Sodium carbonate		Stirrer	1
Calcium chloride		Adapter, three-mouth	1
		Funnel, separatory	1
		Condenser, air	1
		Thermometer	1
		Receivers	2

Assembly

1. A 250-ml round-bottom flask is fitted with a three-mouth adapter, one neck of which is closed with a stopper having a thermometer that almost reaches the bottom of the flask. A reflux air condenser (which prevents benzene from being volatilized) is inserted in another neck, and a mechanical stirrer, into the third.

2. A nitrobenzene distillation apparatus consisting of a 100-ml Würtz flask, a thermometer and an air condenser turned downwards (it is better to distil nitrobenzene under vacuum) is assembled.

Procedure

Work must be done *in a fume cupboard*! Twenty millilitres of concentrated nitric acid are poured into the reaction flask of apparatus 1 and 25 ml of concentrated sulphuric acid (wear *safety glasses*!) are carefully added while cooling the flask outside with cold water and stirring the mixture.

The benzene is added in 2-3 ml portions through the upper opening of the condenser to the acid mixture cooled to 15°C while stirring. The temperature of the mixture should not rise higher than 50°C; otherwise, a large amount of dinitrobenzene may be formed. The temperature is controlled by the rate at which benzene is added and, when need be, the flask is cooled from time to time by immersing it in a cold water bath and stopping the benzene supply. A brown colour (nitric oxide) often appears when another portion of benzene is added. The rate of benzene addition should be such that brown vapours of nitric oxide are not formed.

The reaction mixture is a heterogeneous system, and therefore nitration occurs only at the acid-benzene interface. If the reaction is to be carried out successfully, the mixture should be thoroughly stirred. This engenders an emulsion, which ensures close contact between the reagents.

When all the benzene has been added, the flask is immersed in a water bath heated to not higher than 60 °C, and the reaction is carried out at this temperature for 30-45 min while continuing to stir the mixture. The reaction mixture is then cooled and poured into a separatory funnel. The liquid is allowed to separate into layers and the lower acid layer is removed from the upper nitrobenzene layer (the acid mixture must not be poured into the drain without first neutralizing it with lime). The nitrobenzene is washed with water, while shaking it not too vigorously, in a separatory funnel to prevent a stable emulsion from being formed. If an emulsion is formed, a drop of alcohol is added, thus changing surface tension.

After the mixture is allowed to stand, the lower nitrobenzene layer is discharged through a stopcock, while the aqueous layer is poured out of the upper opening of the funnel. Nitrobenzene is then poured into the separatory funnel again and, to cleanse it of acid traces, is washed with a dilute sodium carbonate solution until carbon dioxide is no longer liberated (do not close the upper opening of the separatory funnel!). After washing, the lower nitrobenzene layer is discharged into a dry, conical 50-ml flask and dried over anhydrous granulated calcium chloride.

If a layer of an aqueous calcium chloride solution is formed at the bottom of the flask, nitrobenzene is carefully poured into a dry flask, granulated calcium chloride is again added to it and it is dried in the way described above.

To accelerate the drying process, the flask is closed with a stopper, in which a glass tube (which acts as a reflux air condenser) is inserted, and is heated in a water bath for 30 min until the liquid becomes quite clear. The conical flask is shaken from time to time.

The dried nitrobenzene is poured into a 100-ml Würtz flask. Afterwards, apparatus 2 is assembled. The Würtz flask is heated in an air bath or on an asbestos gauze. A small amount of unreacted benzene is driven off at first, and then nitrobenzene is collected at 207-211 °C. The nitrobenzene yield is about 21 g.

Nitrobenzene and other nitro compounds *must not be distilled to dryness*, because di- and polynitro compounds (in this case, dinitrobenzene) can *spontaneously burst into flame* and even *explode*. Distillation should be stopped while the flask still has some liquid or when the boiling point reaches 214 °C.

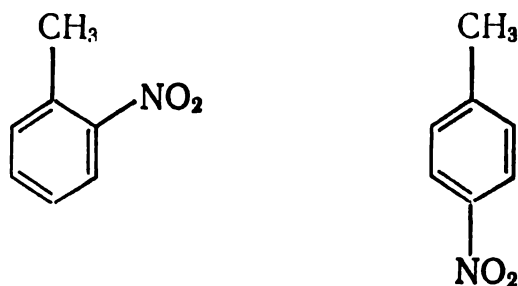
Nitrobenzene (oil of mirbane) is a slightly yellowish oily liquid with a bitter almond odour. Its molecular weight is 123.11; b.p., 210.9 °C; d_{20}^{20} , 1.2055, and n_D^{20} , 1.5525. It dissolves in alcohol, benzene and ether, but is almost insoluble in water. Nitrobenzene *poisons* the central nervous system and upsets metabolism, causing liver diseases. Its vapours cause *headache* when they are inhaled for a long time; and nitrobenzene causes *burns* when it gets on the skin. The lesion should be rubbed with alcohol and then washed with soap and water.

Nitrobenzene is used for obtaining aniline, benzidine, *m*-dinitrobenzene and *m*-dinitrochlorobenzene and for producing dyes. It is also employed as a solvent and for other purposes.

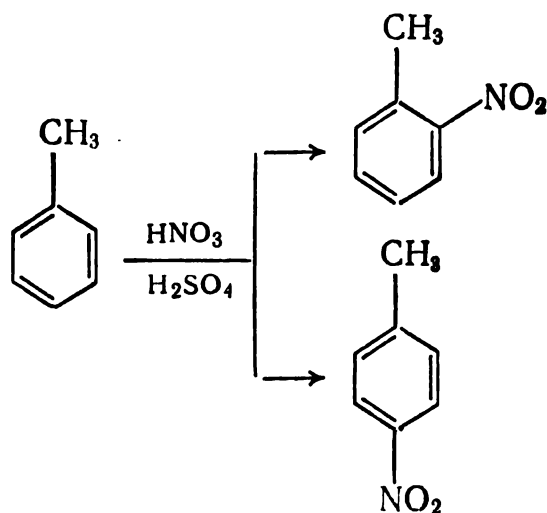
Characterization Test. Nitrobenzene is detected qualitatively by reducing it to aniline and oxidizing the latter with a dilute solution of chlorinated lime or sodium hypochlorite. An intense violet colour originates as the aniline formed is oxidized.

o-, *p*-NITROTOLUENE

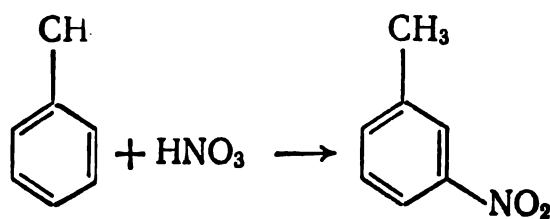
Formulas:



Main reaction:



Side reaction:



Toluene is nitrated more readily than benzene and, according to the substitution rule, a mixture of *o*- and *p*-nitrotoluenes is mainly formed.

Reagents and Equipment

Toluene	23 g or 27 ml (0.24 mole)	Flasks, round-bottom (100 and 200 ml)	2
Nitric acid ($d = 1.4$) . .	25 g or 18 ml (0.25 mole)	Funnel, dropping	1
Sulphuric acid ($d = 1.84$)	21.5 ml (0.39 mole)	Funnel, separatory	1
Calcium chloride, granulated		Flask, conical	1
		Thermometer for 360 °C	1
		Flask, Würtz (100 ml)	1
		Condenser, air	1
		Beaker (100 ml)	1
		Apparatus, suction	1
		Condenser, Liebig	1
		Receivers	3

Assembly

1. A 200-ml round-bottom flask fitted with both a thermometer for 360 °C, which almost reaches the bottom of the flask, and a dropping funnel is placed in a water bath.

2. An apparatus for distilling unreacted toluene is assembled. A 100-ml Würtz flask is connected to a Liebig condenser and a thermometer.

3. Suction apparatus (see Fig. 2.21).

4. An apparatus for distilling *o*- and *p*-nitrotoluenes. A 100-ml Würtz flask is connected to an air condenser and a thermometer for 360 °C.

Procedure

Work must be done *in a fume cupboard!* The nitrating mixture is prepared in a 100-ml round-bottom flask. Eighteen millilitres of nitric acid are poured into the flask and 21.5 ml of concentrated sulphuric acid (wear *safety glasses!*) are gradually added in small portions while shaking the flask.

Twenty-seven millilitres of pure toluene are poured into the round-bottom flask of apparatus 1 and a nitrating mixture is added in 1-2 ml portions through the top of the air condenser while stirring the contents of the flask. The mixture is poured in at such a rate that the temperature of the reaction mixture will not rise above 60 °C. If the temperature does rise above 60 °C, the flask should be cooled with cold water to preclude the formation of by-products, polynitro derivatives.

When all the nitrating mixture has been added, heat the flask in a water bath at 60 °C for 30 min. The reaction mixture is then cooled and transferred to a separatory funnel. Allow the liquid to

separate into layers. The lower layer consisting of sulphuric and nitric acids is removed. The upper layer is washed with water. After allowing the oily lower layer to settle, the liquid is poured into a dry conical flask and dried with granulated calcium chloride until it becomes clear.

Apparatus 2 is then assembled and the liquid is distilled by heating it on a gauze to 150 °C. The unreacted toluene will thus be driven off; part of the toluene is not used in the process as a result of nitration at low temperature. After distillation, the residue is transferred to a 100-ml beaker and allowed to stand in a cooling mixture of ice and salt for 10-12 hours. *p*-Nitrotoluene crystals are then formed, which are sucked off in the Büchner funnel and driven off (apparatus 4) at 232-238 °C (nitrotoluene must not be distilled to dryness; otherwise an *explosion* can occur!).

The oily layer is distilled (with the same apparatus) at 216-222 °C.

o-, *p*-Nitrotoluenes are most thoroughly separated by vacuum fractional distillation. The *o*- and *p*-nitrotoluene yield is 30-31 g.

About 4 per cent of *m*-nitrotoluene is formed together with *o*- and *p*-nitrotoluenes.

o-Nitrotoluene is a light yellow liquid which dissolves well in alcohol and ether. Its molecular weight is 137.14; b.p., 222.3 °C; and n_D^{20} , 1.5472.

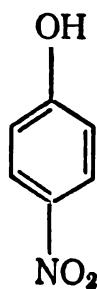
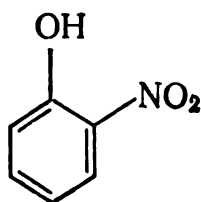
p-Nitrotoluene consists of colourless crystals which dissolve well in alcohol and ether. It boils at 238 °C and melts at 57 °C.

o-, *p*-Nitrotoluenes are used for producing dyes and carrying out analyses, and are also employed as intermediates. Nitrotoluenes are *poisonous* because they oxidize hemoglobin into metahemoglobin.

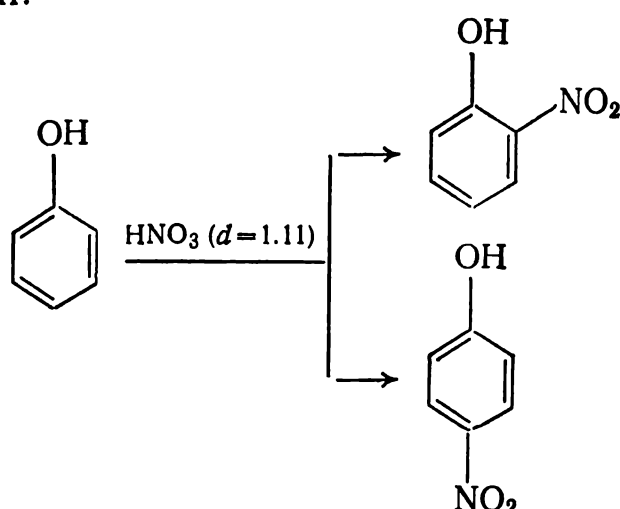
Characterization Test. Two millilitres of nitrotoluene and 5 ml of petroleum ether are poured into a test tube. Afterwards 0.5 g of powdery potassium hydroxide is added while vigorously shaking the test tube. A yellow-brown colour appears.

o-,*p*-NITROPHENOL

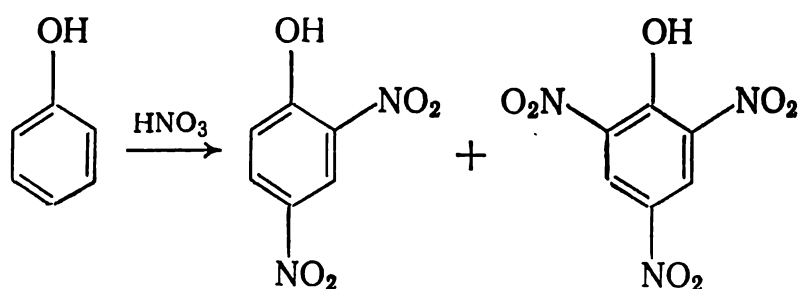
Formulas:



Main reaction:



Side reaction:



Phenol is nitrated very readily by dilute nitric acid ($d = 1.11$) even in the cold, forming *o*- and *p*-nitrophenol. Since the nitronium ion is absent in dilute nitric acid, phenols are nitrated by the preliminary formation of nitrozophenol with its subsequent oxidation to nitrophenol by nitric acid.

Reagents and Equipment

Phenol	28.2 g (0.3 mole)	Flask, round-bottom (300 ml) . . .	1
Nitric acid ($d = 1.11$) .	185 ml (0.6 mole)	Flask, conical (150 ml)	1
Ethyl alcohol		Thermometer for 100 °C	1
Activated charcoal		Apparatus, steam distillation . . .	1
Hydrochloric acid, 2 per cent		Apparatus, suction	1
		Apparatus, recrystallization . . .	1

Assembly

1. Steam distillation apparatus (see Fig. 3.6).
2. Suction apparatus (see Fig. 2.21).

Procedure

Put 28.2 g of phenol and 5 ml of water in the 150-ml conical flask, and heat the contents until they melt. Afterwards 185 ml of nitric acid are poured into the 300-ml round-bottom flask and molten phenol is gradually added while continuously shaking the

flask and stirring its contents. The temperature of the reaction mixture must not top 20 °C. Otherwise, di- and trinitrophenols may be formed.

When all the phenol has been put in, this dark mixture is placed in icy water for two or three hours, frequently shaking the flask vigorously. The mixture is then poured into water, whose volume is double that of the mixture, and allowed to stand until an oily, partially resinified reaction product separates from the aqueous layer and precipitates to the bottom of the flask. The water layer is carefully decanted, while the residue is washed with water two or three times in order to remove nitric acid traces.

When dilute nitric acid is used as a nitrating agent, resinous by-products of oxidation and polymerization are formed, reducing the yield of the reaction product. It is therefore better to nitrate phenol with a mixture of sodium or potassium nitrate and concentrated sulphuric acid in an aqueous solution.

After being washed, the oily layer is transferred to a 500-ml flask for steam distillation. Only *o*-nitrophenol is driven off as yellow, rapidly crystallizing oil. The *p*-nitrophenol, not driven off with steam, remains in the flask. Distillation is complete when a sample (several millilitres of the distillate) will not form crystals when it cools.

The receiver must be cooled with cold water. If *o*-nitrophenol begins to crystallize in the condenser, clogging up the inner tube, stop the water supply to the condenser for a while. The hot condensate will then melt the solidified product which drips into the receiver. Afterwards, water should be let gradually into the condenser; otherwise, the condenser may burst.

The precipitated *o*-nitrophenol crystals are sucked off in the Büchner funnel, squeezed between sheets of filter paper and air-dried (*o*-nitrophenol is very volatile and must not be dried in a drier).

If the *o*-nitrophenol obtained is not quite pure, any impurity being judged by a dark colour and an inconformity of its melting point, it should be redistilled with steam or recrystallized from dilute alcohol.

Recrystallization from dilute alcohol is carried out in the following way: *o*-nitrophenol is dissolved in a small amount of boiling alcohol in a flask fitted with a reflux air condenser. Hot water is carefully added dropwise while stirring the mixture until it is faintly turbid. Add several more drops of hot alcohol until the turbidity disappears, and then quickly cool the solution. The pure *o*-nitrophenol crystals which have precipitated are filtered off in the Büchner funnel and dried between sheets of filter paper.

The *p*-nitrophenol (which remains in the flask after *o*-nitrophenol has been driven off with steam) is cooled, separated from the water and transferred to a flask containing 350 ml of a 2 *N* sodium hydroxide solution, into which finely ground, activated charcoal is also added and the mixture is then boiled and filtered

off. The filtrate is boiled down in a water bath until a drop of the solution solidifies on cooling. Add 30 ml of a 30 per cent sodium hydroxide solution and cool the mixture. The isolated sodium *p*-nitrophenolate is sucked off and washed several times with large amounts of a 10 per cent sodium hydroxide solution in a funnel.

The preparation obtained is transferred to a beaker and decomposed with 10 per cent hydrochloric acid while heating the contents of the beaker. The oily *p*-nitrophenol which has separated solidifies on cooling. It is removed and recrystallized from hot, 2 per cent hydrochloric acid, as a result of which colourless needles are formed. The yield of *o*-nitrophenol is about nine grams, and that of *p*-nitrophenol, about four grams.

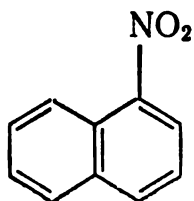
o-Nitrophenol is a yellow crystalline substance with a pungent aromatic odour. It dissolves sparingly in cold water and well in hot water, alcohol and ether. Its molecular weight is 139.11; b.p., 217 °C; m.p., 45 °C, and d_4^{60} , 1.2712. *o*-Nitrophenolates are orange-red.

p-Nitrophenol consists of odourless, colourless crystals which dissolve well in hot water, alcohol and ether. Its b.p., is 279 °C (dec.); m.p., 114 °C, and d_4^{20} , 1.480. *p*-Nitrophenolates are yellow. Nitrophenols are used for producing sulphur dyes, explosives, insecticides and herbicides. *p*-Nitrophenol is employed also as an indicator for colorimetrically determining pH.

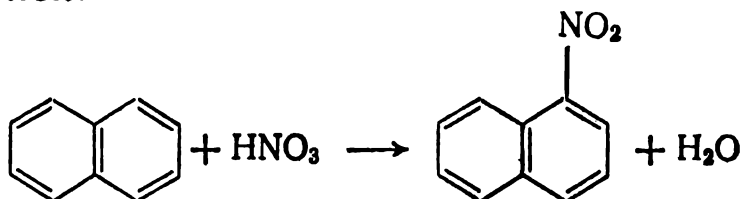
Characterization Test. *p*-Nitrophenol, unlike *o*-nitrophenol, when mixed with ferric chloride produces a red-violet colour.

α -NITRONAPHTHALENE

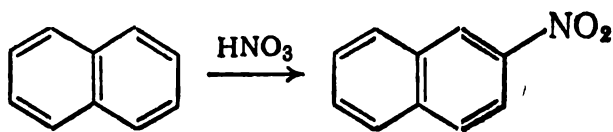
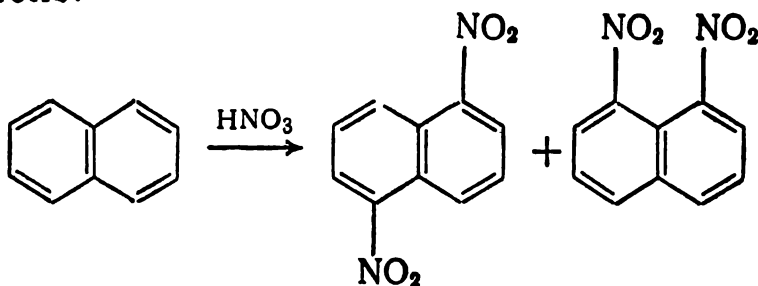
Formula:



Main reaction:



Side reactions:



Hydrocarbons of the naphthalene series are nitrated more readily than those of the benzene series. When naphthalene is being nitrated, the nitro group takes mainly the α -position (β -nitrophenol is formed in very small quantities).

Reagents and Equipment

Naphthalene	16.6 g (0.13 mole)	Beakers (200 and 500 ml) . .	2
Nitric acid ($d = 1.4$) . . .	25 g or 18 ml (0.25 mole)	Thermometer	1
Sulphuric acid ($d = 1.84$) .	14.3 ml	Apparatus, suction	1
Alcohol			

Assembly

1. A 200-ml beaker, placed in a cold water bath, is fitted with a thermometer which almost reaches the bottom of the beaker.
2. Suction apparatus (see Fig. 2.21).

Procedure

Eighteen millilitres of nitric acid are poured into the 200-ml beaker and 14.3 ml of sulphuric acid are carefully added while cooling and stirring the contents of the beaker. Afterwards, while stirring, 16.6 g of finely ground naphthalene are added in small portions to the acid mixture. The rate at which naphthalene is added is such that the temperature of the reaction mass will not rise higher than 50 °C. When need be, the beaker is cooled with running water.

1. Since naphthalene is nitrated at a temperature below its melting point, it must be thoroughly ground before the reaction. Otherwise, the yield will be smaller.

2. If the temperature conditions are not maintained, a large amount of 1,5- and 1,8-dinitronaphthalenes may be formed together with α -nitronaphthalene.

When all the naphthalene has been added, the reaction mass is allowed to stand for one hour at 60 °C while continuously stirring the contents of the beaker. Afterwards, it is poured into a 500-ml beaker containing 200 ml of cold water. The α -nitronaphthalene will solidify in the form of a cake which floats on the solution surface. The water-acid layer is poured out, while the crude α -nitronaphthalene is boiled several times (for 15 min every time) in a beaker containing 100 ml of water. Water is decanted whenever the crude α -nitronaphthalene is boiled. The product is boiled until the liquid no longer shows an acid reaction. While vigorously stirring, molten α -nitronaphthalene is poured out in a thin stream into a beaker containing 200 ml of cold water. It solidifies into reddish-yellow spherules in the beaker.

The precipitate is filtered off in the Büchner funnel, squeezed between sheets of filter paper and dried in the air. To obtain a pure product, it is recrystallized from dilute alcohol. α -Nitronaphthalene is recrystallized from alcohol in the same way as *o*-nitrophenol (see p. 228). The α -nitronaphthalene yield is about 20 g.

α -Nitronaphthalene consists of yellow needle crystals. It is insoluble in water, but dissolves well in alcohol, ether and carbon disulphide. Its molecular weight is 173.17; b.p., 304 °C, and m.p., 61.5 °C.

It is used for producing dyes and obtaining naphthylamine.

Characterization Test. α -Nitronaphthalene with dimethylaniline produces a blood-orange colour.

Chapter 13

AMINATION REACTIONS

Amines can be regarded as the products of the replacement of one, two or three hydrogens in ammonia by organic radicals.

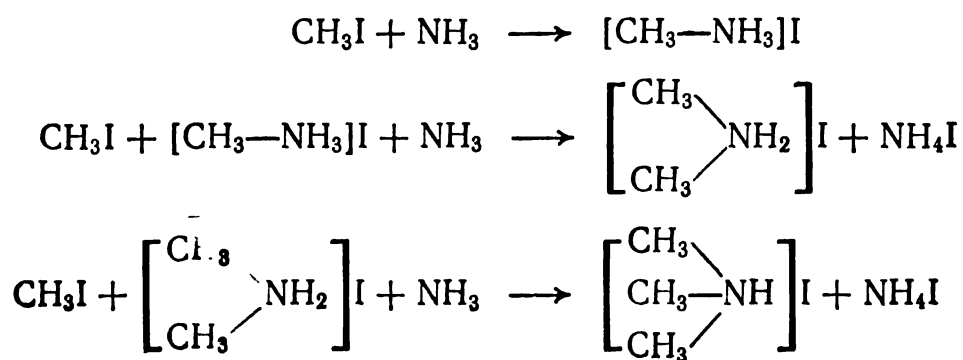
There are primary $R-NH_2$, secondary $\begin{array}{c} R \\ \diagdown \\ NH \\ \diagup \\ R' \end{array}$ and tertiary $\begin{array}{c} R \\ \diagdown \\ R'-N \\ \diagup \\ R'' \end{array}$

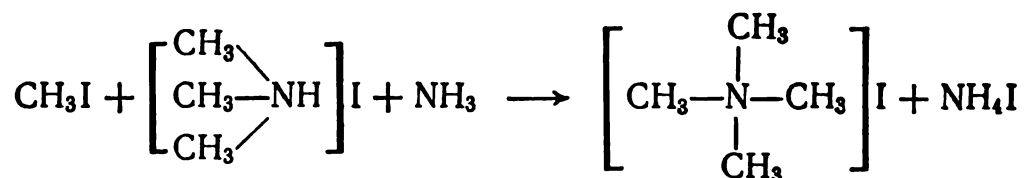
amines, respectively. Amines can be of the fatty, alicyclic, aromatic, heterocyclic or mixed series, depending on the nature of the radicals attached to the nitrogen atom.

Amines possess basic properties, i.e., they are capable of producing salts when they react with acids. Even sparingly water-soluble amines, whose basicity cannot be determined with an indicator, form salts when they react with mineral acids. Therefore, they can be distinguished from neutral nitrogen-containing substances, e.g., amides and nitriles, by a simple acid test. Amines are a very important class of compounds because they are intermediates in the production of many medicinals (such as sulphanilamide preparations and *p*-aminosalicylic acid, PASA), dyes, high molecular weight compounds (polyvinylcarbazole), etc.

13.1. PREPARATION OF AMINES OF THE FATTY SERIES

One of the main methods of synthesizing amines of the fatty series, i.e., Hofmann's reaction, consists in the interaction between halogen derivatives and ammonia which simultaneously leads to the formation of a mixture of amines and a quaternary ammonium salt. For instance, methyl iodide gives a mixture of the salts of mono-, di- and trimethylamine and tetramethylammonium:





Primary, secondary and tertiary amines of the fatty series are now obtained industrially through the interaction between alcohols and ammonia over aluminium oxide. Primary amines can be obtained also by treating acid amides by bromine and alkali.

Primary amines are occasionally obtained by reducing nitriles, oximes, azides, nitroso compounds, and hydrazones.

Nitrous acid is used for detecting and separating amines of the fatty series. When nitrous acid acts on primary amines of the fatty series, nitrogen is liberated and the corresponding alcohol is formed. Secondary fatty amines with nitrous acid give nitrosamines (R_2NNO), while the tertiary amines remain unchanged at room temperature.

13.2. PREPARATION OF AMINES OF THE AROMATIC SERIES

Many aromatic amines are obtained by reducing the corresponding nitro compounds with hydrogen *in situ*:



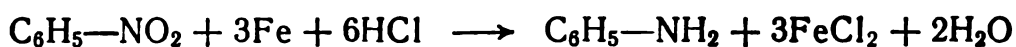
The reaction of reducing nitrobenzene to aniline was first studied by N.N. Zinin in 1841. He used ammonium sulphide as the reducing agent:



This discovery was exceptionally important in the development of organic chemistry, especially in the production of dyes, medicine and photographic reagents.

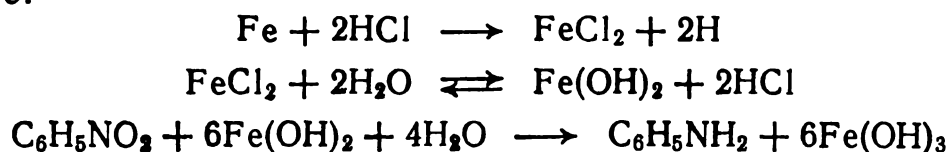
The reagents now used are iron and hydrochloric or sulphuric acid, tin and hydrochloric acid, hydrogen sulphide and sulphur alkalies, bisulphites, and catalytically excited hydrogen. Moreover, reduction can be carried out electrolytically.

Different products can be obtained as a result of reduction, depending on the nature of the medium. Aromatic amines are usually obtained as end products in the acid medium. An important industrial method now used is the reduction of nitrobenzene by hydrogen *in situ* in the acid medium, e.g., by iron (tin, zinc) and hydrochloric acid:



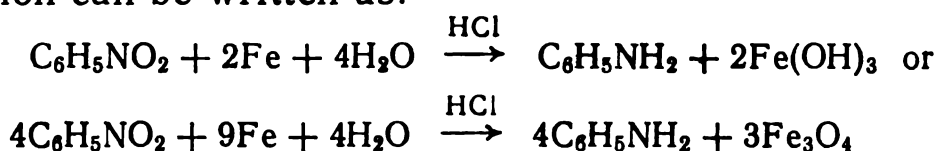
To carry out the reaction, considerably less acid is used than required by the equation because, together with the main reaction,

ferrous chloride is hydrolyzed with the formation of hydrochloric acid and ferrous hydroxide. Ferrous hydroxide readily reduces nitrobenzene to aniline, and is simultaneously oxidized to ferric hydroxide:

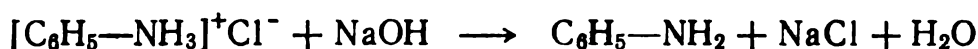


A mixed iron oxide, Fe_3O_4 , can also originate in the reaction medium.

Thus, acid acts as the initiator of the reaction. On the whole, the reaction can be written as:



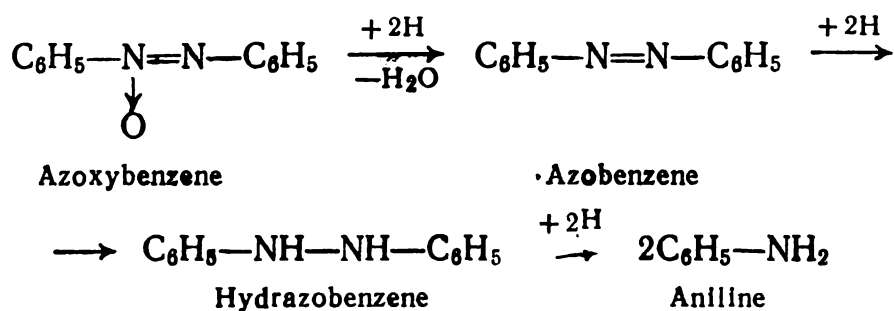
Aniline forms a salt with hydrochloric acid which, after reduction, is decomposed by adding sodium carbonate or alkali:



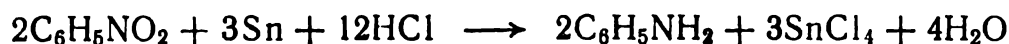
Nitrosobenzene and phenylhydroxylamine are formed as intermediates.

Intermediates cannot be separated when a reaction is carried out in an acid medium. In a neutral medium, phenylhydroxylamine can be obtained, e.g., under the action of zinc in the presence of ammonium chloride. When it is heated, it isomerizes to *p*-aminophenol.

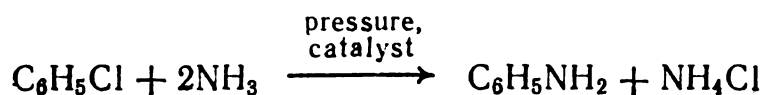
The process is more complicated in an alkaline medium. The intermediates, i.e., nitrobenzene and phenylhydroxylamine, interact, forming azoxybenzene (an azoxy compound), next an azo compound (azobenzene) and a hydrazo compound (hydrazobenzene), and finally amine:



Reduction by tin is not used industrially because tin is very expensive. This method is widely used in laboratories, however, because tin is a very strong reducing agent. The summary equation for the reduction of nitrobenzene by tin in an acid medium is:



Aromatic amines are obtained in most cases from the halogen derivatives of the aromatic series and ammonia:



Since the halogen atom attached to the aromatic ring is not very mobile, the reaction must be carried out in autoclaves at high pressures and temperatures in the presence of catalysts (copper and its compounds).

A good way of obtaining pure secondary fatty amines is by nitrosating dialkylanilines with the subsequent hydrolysis of the reaction product:



Due to the effect of the phenyl group, the main properties of aromatic amines are far less pronounced than those of amines of the fatty series. Almost all the aromatic amines are unstable if they are not absolutely pure. They become grey, violet or black apparently as a result of oxidation.

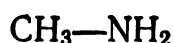
Aromatic amines can be purified in the following way: amine is dissolved in dilute hydrochloric acid at 50°C, 10 per cent (with respect to the amine mass) of stannous chloride is added, and hydrogen sulphide is passed through the mixture until tin completely precipitates. To precipitate the flaky stannous sulphide, a small amount of sodium chloride is added to the mixture. The sulphur compounds are filtered off, and, to remove hydrogen sulphide, the filtrate is boiled and alkalized. If the amine is sparingly soluble, it is filtered off; if it is readily soluble or is a liquid, it is extracted with ether.

The aromatic amines thus purified can be stored for a long time without any change.

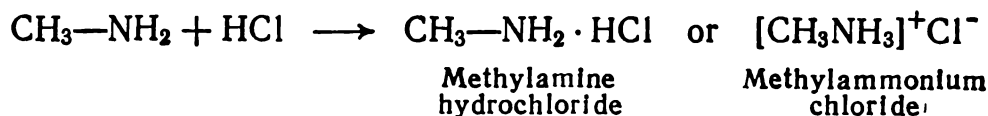
13.3. SYNTHESSES

METHYLAMINE

Formula:



Main reactions:



Reagents and Equipment

Acetamide	15 g (0.25 mole)	Flask, round-bottom, two-necked (500 ml)	1
Bromine	13 ml (0.26 mole)	Flask, Würtz (150 ml)	1
Sodium hydroxide	65 g	Funnel, dropping	1
Hydrochloric acid (<i>d</i> = 1.19) .	40 ml	Condenser, air	1
Alcohol, absolute		Thermometer	1
		Apparatus, steam distillation . . .	1
		Flask, Bunsen	1
		Funnel, Büchner	1
		Dish, porcelain	1

Assembly

1. A 500-ml round-bottom, two-necked flask is immersed in a water bath and fitted with a dropping funnel and a reflux air condenser. A thermometer, whose end is immersed in a water bath, is secured in the stand claw.

2. Steam distillation apparatus (see Fig. 3.6). A bent adapter is connected to the condenser, and its end is immersed by 1 cm in hydrochloric acid in a receiver.

3. Suction apparatus (see Fig. 2.21).

Procedure

Work must be done *in a fume cupboard*! Fifteen grams of acetamide and 13 ml of bromine are mixed in the round-bottom flask of apparatus 1 (see p. 15). While shaking the mixture and cooling it well in water, a solution of 25 g of potassium hydroxide in 175 ml of water is gradually added until the red-brown colour of the solution becomes light yellow, i.e., until the bromine colour disappears.

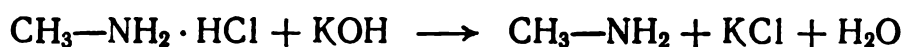
Apparatus 1 is assembled. The solution obtained is slowly added through a dropping funnel to a solution of 40 g of potassium hydroxide in 75 ml of water, which is in the 500-ml flask. Afterwards, the reaction mixture is heated in a water bath at 70-75 °C, making sure that it is not superheated. The mixture is heated until it is decolorized (15-30 min).

The methylamine formed is driven off with steam and collected as hydrochloride in a receiver containing 30 ml of concentrated hydrochloric acid and 20 ml of water. Distillation is stopped when the condensate in the condenser no longer gives an alkaline reaction. The contents of the receiver are transferred to a porcelain dish and boiled down to dryness in a water bath. For complete drying, the dish containing the dry residue is allowed to stand for 10-12 hours, either in a vacuum desiccator or in a drying cabinet at 100 °C.

To separate ammonium chloride from methylamine hydrochloride, the dry residue is finely ground and boiled with absolute alcohol (see p. 41); the ammonium chloride will not dissolve. After filtering off the ammonium chloride precipitate, the clear filtrate containing methylamine hydrochloride is boiled down in a water bath so that a small amount remains. Afterwards, the solution is rapidly cooled and the soft methylamine hydrochloride crystals which have precipitated are sucked off in the Büchner funnel, washed with a small amount of alcohol and dried in a desiccator. The methylamine hydrochloride yield is 7-10 g.

Free methylamine can be isolated under the action of alkali on methylamine hydrochloride. Three grams of methylamine hydro-

chloride are put in a 150-ml Würtz distilling flask, which is closed with a stopper having a dropping funnel inserted in it. The outlet tube of the flask is connected to a bent glass tube by means of rubber tubing. Afterwards, 35 ml of a 50 per cent potassium hydroxide solution are added from the dropping funnel and the mixture is carefully heated. Free methylamine is evolved in the form of a gas with a characteristic strong odour:



Methylamine hydrochloride is a white crystalline powder. It is readily soluble in water and alcohol, but is insoluble in ether, acetone and chloroform. Its molecular weight is 67.52; b.p., 225-230 °C at 15 mm Hg, and m.p., 227-228 °C (sublimation).

Methylamine is a gas with a strong nauseating odour. It is highly flammable and readily mixes with alcohol, ether and benzene. It is produced industrially in the form of hydrochloride or aqueous solutions. Its molecular weight is 31.06; b.p., -6.5 °C; m.p., -93.6 °C, and d_4^{-11} , 0.696. Methylamine is poisonous, being oxidized in the organism with the formation of formic acid. Moreover, it oppresses the respiratory functions.

It is used for producing pharmaceuticals, dyes of the anthraquinone series, photographic reagents and surfactants, as well as being employed for other purposes.

To identify the primary amines of the fatty series, the following reactions are carried out:

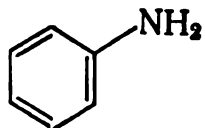


An amount of 0.5 g of methylamine hydrochloride is dissolved in 2 ml of water, and then 2-3 ml of a 10 per cent sodium nitrite solution are added. In this case, nitrogen bubbles are formed.

Characterization Test. Primary amines give a violet colour when sodium nitroprusside and acetone are added to them.

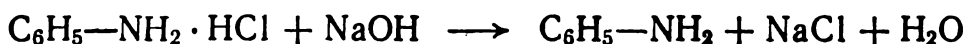
ANILINE

Formula:



*Reduction of Nitrobenzene with Iron in the Presence of Acid **

Main reactions:



* To spend less time, carry out the synthesis by using a large amount of hydrochloric acid.

Reagents and Equipment

Nitrobenzene	18 g or 15 ml (0.15 mole)	Flask, round-bottom (500 ml)	1
Hydrochloric acid ($d = 1.19$)	80 ml (1 mole)	Flask, distilling (250 ml)	1
Iron (filings)	30 g (0.55 gram atom)	Funnel, separatory (500 ml)	1
Sodium hydroxide	45 g	Condenser, air	1
Ethyl ether	120 ml	Condenser, Liebig	1
Potassium hydroxide	5 g	Thermometer	1
Sodium chloride		Adapter, bent	1
		Apparatus, steam distilla- tion	1

Assembly

1. A 500-ml round-bottom flask, fitted with an air condenser, is placed in a water bath.
2. Steam distillation apparatus (see Fig. 3.6).
3. A 250-ml distilling flask, fitted with a thermometer, is connected to an air condenser on whose end is a bent adapter (a water condenser is used for distilling ether).

Procedure

Work must be done *in a fume cupboard!* Fifteen millilitres of nitrobenzene and 30 g of iron filings are put in the flask of apparatus 1, and 80 ml of hydrochloric acid are added in 1-2 ml portions.

Prior to reduction, it is expedient to boil the iron with acid to make it more active. In this case, the thin oxide film on the iron surface dissolves.

The contents of the flask are stirred well whenever a portion of acid is added. If the reaction occurs too vigorously, cool the flask in cold water. When half of the hydrochloric acid has been added, introduce the other half in large portions (10-20 ml). The flask is then heated in a water bath for 30 min.

The reaction is complete when the characteristic odour of the nitrobenzene disappears and part of the iron turns into red-brown ferriferrous oxide. Next, 30 ml of water are carefully added to the hot reaction mixture, and then a solution of 45 g of sodium hydroxide in 60 ml of water is introduced in small portions until an alkaline reaction occurs.

The aniline separated is steam distilled from the hot liquid. An aqueous aniline emulsion collects in the receiver and separates into layers. The receiver is changed when a cloudy liquid flows from the condenser. Distillation is carried on until the distillate becomes quite clear. The lower aniline layer which collects at the bottom

of the first receiver is separated in a separatory funnel, while the upper layer is mixed with the contents of the second receiver. Aniline is salted out from the combined distillate by finely ground sodium chloride, adding 20 g of sodium chloride per 100 ml of the distillate.

Aniline dissolves sparingly in water (three grams of aniline dissolve in 100 g of water). To separate it more thoroughly from the aqueous solution, the distillate is saturated with sodium chloride, in whose concentrated solution aniline does not dissolve.

After sodium chloride dissolves, the oily aniline layer is separated in a separatory funnel and added to the first portion, while the aqueous layer is treated with ether (see p. 63). The ethereal extract is added to the aniline separated earlier and dried with several pieces of solid potassium hydroxide (to this end, use can also be made of calcium oxide, barium oxide and soda lime; calcium chloride is not used for drying amines because together they form crystal-hydrate type compounds. Ether is then driven off with a water condenser in a water bath. Afterwards, aniline is distilled with an air condenser on a gauze (for decolorization purposes, aniline can be distilled over a small amount of zinc dust), and the fraction which boils at 184°C is collected. The aniline yield is about 11 g.

Reduction of Nitrobenzene with Iron in the Presence of a Small Amount of Hydrochloric Acid

Reagents and Equipment

Nitrobenzene	31 g or 25.7 ml (0.25 mole)	Flask, round-bottom (1000 ml)	1
Iron (filings)	60 g (1.1 gram atom)	Flask, distilling (500 ml)	1
Hydrochloric acid ($d=1.19$)	10 ml (0.13 mole)	Funnel, dropping	1
Sodium carbonate	7-10 g	Head, still	1
Ethyl ether	50 ml	Condenser, Liebig	1
Sodium chloride		Funnel, separatory	1
Potassium hydroxide		Thermometer	1
		Adapter, bent	1
		Apparatus, steam distillation	1

Assembly

1. A 1000-ml round-bottom flask, placed in a sand bath, is connected to a still head which is fitted with a dropping funnel and a reflux water condenser. For stirring purposes, the condenser is connected to an adapter by rubber tubing.

2. Steam distillation apparatus (see Fig. 3.6).

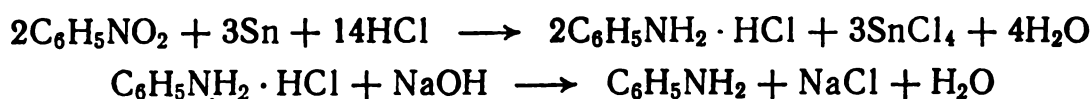
3. Apparatus 3 on p. 238.

Procedure

Work must be done *in a fume cupboard!* Sixty grams of fine iron filings, 75 ml of water and 26 ml of nitrobenzene are put in the round-bottom flask of apparatus 1. Next, 10 ml of hydrochloric acid are poured in through the top of the condenser. Nitrobenzene is reduced to aniline by heating the mixture in a sand bath for 4-4.5 hours. After completing reduction, 7-10 g of sodium carbonate (or the same amount of alkali) are added to the reaction mixture and aniline is steam distilled. Work is then done as indicated on pages 238-239. The aniline yield is about 18 g.

Reduction of Nitrobenzene with Tin in the Presence of Hydrochloric Acid

Main reactions:



Reagents and Equipment

Nitrobenzene	18.5 g or 15 ml (0.15 mole)	Flask, round-bottom (500 ml)	1
Tin, granulated	36 g (0.3 gram atom)	Flask, distilling (250 ml)	1
Hydrochloric acid ($d = 1.19$)	80 ml (1 mole)	Funnel, separatory (500 ml)	1
		Condenser, air	1
		Condenser, Liebig	1
		Apparatus, steam distillation	1
		Adapter, bent	1
Sodium hydroxide	45 g		
Ethyl ether	120 ml		
Potassium hydroxide	5 g		
Sodium chloride			

Assembly

1. A 500-ml round-bottom flask is placed in a water bath and fitted with an air condenser.
2. Steam distillation apparatus (see Fig. 3.6).
3. A 250-ml distilling flask is connected to a thermometer and to an air condenser (a water condenser is used for distilling ether) on whose end is a bent adapter.

Procedure

Work must be done *in a fume cupboard!* Thirty-six grams of granulated tin and 15 ml of nitrobenzene are put in the round-bottom flask of apparatus 1.

If there is no granulated tin in the laboratory, it can be made by melting pieces of tin in an iron spoon with a wooden handle over a burner flame. The molten mass is then poured dropwise, from a height of 1.5 m, into a bucket filled with water.

Ten millilitres of concentrated hydrochloric acid are gradually and carefully added to the mixture. The contents of the flask are shaken well. Somewhat later, the mixture will become warm and begin to boil owing to the heat of reaction. Cool the flask with cold water, but so as not to terminate the reaction. Then, 70 ml of the remaining hydrochloric acid are gradually added in small portions while continuously shaking the flask. The mixture must boil vigorously.

When all the acid has been added, the flask is heated for another hour in a water bath, making sure that it boils slightly. A solution of 45 g of sodium hydroxide in 90 ml of water is then carefully added in small portions to the still hot solution until a strongly alkaline reaction occurs which neutralizes hydrochloric acid and decomposes aniline hydrochloride. The flask is then connected to the steam distillation apparatus. Aniline is distilled together with water. It collects in the form of light yellow oily drops at the bottom of the receiver. Work is carried on further as described on pages 238-239. The aniline yield is about 12 g.

Aniline (aminobenzene) is a colourless or pale yellow liquid with a peculiar odour. It darkens when exposed to light and air. Its solubility is 3.6 g per 100 g of water. It mixes well with alcohol, ether and benzene. Its molecular weight is 93.13; b.p., 184.4 °C; m.p., -6.15 °C; d_4^{20} , 1.0217; and n_D^{20} , 1.5863.

Aniline is very *poisonous to blood*. Poisoning may occur either when liquid aniline gets on the skin or when its vapours are inhaled.

It is used for producing intermediates, dyes and artificial resins and also for obtaining photographic developers and accelerators of rubber vulcanization (mercaptobenzthiazole). It is employed as well in the textile industry (in aniline black dyeing), the pharmaceutical industry (acetanilide, sulphamides and neoarsphenamine) and laboratories.

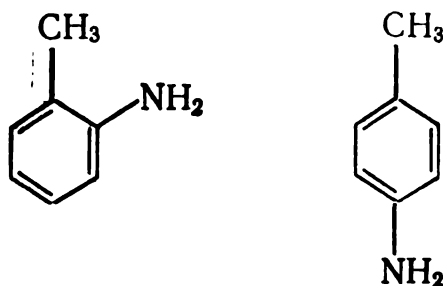
Characterization Tests. 1. Four drops of aniline are dissolved in 10 ml of water, in a test tube, a few drops of hydrochloric acid are added and several small crystals of potassium bichromate and cupric sulphate are dissolved in this mixture. When the mixture is slowly heated, it becomes dark green and black flakes fall out.

2. Two drops of aniline and 20 ml of water are put in a test tube, and 2-3 drops of a chlorinated lime solution are added. A violet colour will appear (unlike *o*-toluidine, which gives a yellowish-brown colour under these conditions).

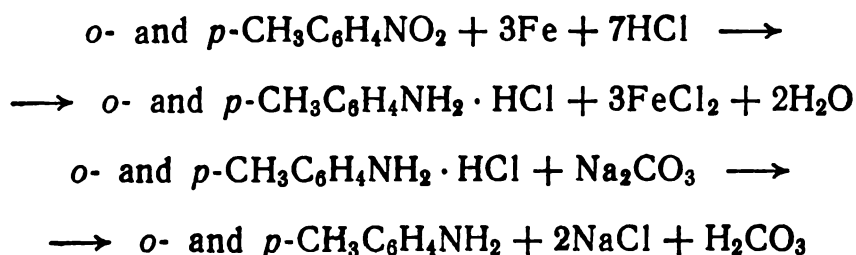
3. A drop of a solution containing aniline hydrochloride is deposited on a piece of newspaper or a piece of napkin (both contain a great deal of lignin). A yellow-orange spot will appear. Filter paper or Whatman paper, which do not contain lignin, will not become coloured.

***o*-, *p*-TOLUIDINE**

Formulas:



Main reactions (see pp. 233-234):

**Reagents and Equipment**

Mixture of <i>o</i> - and <i>p</i> -nitrotoluene .	18 g (0.13 mole)	Flask, round-bottom with three necks (500 ml)	1
Iron (filings) . .	20 g (0.36 gram atom)	Flask, distilling (50 ml)	1
Hydrochloric acid (<i>d</i> = 1.19) . . .	2 ml (0.02 mole)	Condenser, air	1
Sodium carbonate, anhydrous . . .	3 g	Condenser, Liebig	1
Potassium hydro- xide	10 g	Thermometer	1
Benzene	130 ml	Stirrer	1
Zinc dust	0.5 g	Funnel, separatory	1
Sodium hydroxide		Funnel, dropping	1
		Apparatus, steam distillation . . .	1
		Adapter, bent	1
		Receivers	2

Assembly

1. A 500-ml round-bottom flask with 3 necks is fitted with a thermometer, an air condenser and a stirrer. It is placed in a water bath.

2. Steam distillation apparatus (Fig. 3.6).

3. A 50-ml distilling flask is connected to a dropping funnel and to a Liebig condenser fitted with a bent adapter, and is placed in a water bath.

4. A 50-ml distilling flask with a thermometer is connected to an air condenser fitted with a bent adapter, which is lowered into a receiver.

Procedure

Work must be done *in a fume cupboard!* Twenty grams of fine iron filings, 150 ml of water and 2 ml of concentrated hydrochloric acid are put in the round-bottom flask with three necks of apparatus 1. The flask is then heated to 70 °C in a water bath. Then, 1 ml of a mixture of *o*- and *p*-nitrotoluene is poured through the opening into which the air condenser is inserted. The mechanical stirrer is switched on. The temperature of the mixture immediately rises owing to the heat evolved by the reaction. The remaining amount of *o*- and *p*-nitrotoluene is gradually poured in 1-2 ml portions (while vigorously stirring the mixture) through the top of the air condenser at such a rate that the temperature of the reaction mixture does not rise higher than 95 °C. The reaction may be considered complete when a sample of the mixture no longer produces the bitter almond odour characteristic of nitro compounds when dilute hydrochloric acid is added to the sample.

After the reaction, three grams of sodium carbonate are carefully added to the mixture so as to neutralize it and isolate the toluidines from their salts. The steam distillation apparatus is then assembled and the reaction mixture is distilled until a sample of the distillate with a concentrated solution of sodium hydroxide is no longer turbid. Sodium chloride is added to the distillate (20 g of sodium chloride per 100 ml of the distillate) and the flask is shaken until almost all the sodium chloride dissolves. (Sodium chloride is needed for more thoroughly isolating toluidines from the aqueous solution.)

The distillate is decanted from the remaining sodium chloride into a separatory funnel and toluidines are extracted several times with benzene. The combined benzene extracts are dried over potassium hydroxide (see p. 49) and apparatus 3 is assembled. The dried extracts are transferred to a dropping funnel installed in a Würtz flask, and benzene is distilled in a boiling water or a sand bath while gradually pouring the solution from the funnel into the flask. When all the benzene has been driven off, the dropping funnel is replaced with a thermometer (apparatus 4). To decolorize the toluidines, 0.5 g of zink dust is put in the flask and the toluidines are driven off at 194-195 °C over an open flame. The yield of the toluidine mixture is about 11 g.

o-Toluidine is a colourless liquid which darkens when exposed to light and air. It mixes with alcohol, ether and other organic solvents. At 25 °C, 1.5 g of it dissolves in 100 g of water. Its molecular weight is 107.15; b.p., 200.4 °C; m.p., -16.4 °C; d_4^{15} , 1.0028; and n_D^{20} , 1.5728.

p-Toluidine consists of lustrous, colourless flakes. It dissolves well in alcohol, ether and carbon disulphide. At 20 °C, 0.74 g of it dissolves in 100 g of water. Its b.p. is 200.5 °C; m.p., 43.7 °C; d_4^{60} , 0.9538; and n_D^{59} , 1.5532. Toluidines are poisonous,

Toluidines are employed in dye production and laboratory operations. They are also used as additives to motor fuels and for other purposes.

Characterization Tests. *o*-Toluidine. 1. Two drops of *o*-toluidine are dissolved in 2 ml of 50 per cent sulphuric acid. The mixture is then heated to 50°C and three drops of a saturated potassium bichromate solution are added. The mixture is shaken and poured a minute later into 500 ml of water. The solution is stirred until it no longer changes colour. It is then alkalized with ammonia. When bichromate is added, the solution turns reddish and then dark blue. When the solution is diluted with water and stirred, it turns orange-yellow. When it is alkalized with ammonia, it turns blue.

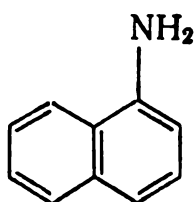
2. When an ethereal solution of *o*-toluidine is shaken together with a dilute chlorinated lime solution, the water layer turns brown.

***p*-Toluidine.** 1. A test with bichromate (see *o*-Toluidine, paragraph 1). When bichromate is added, the solution turns reddish brown. When the solution is diluted with water and stirred, it turns yellow, and when it is alkalized with ammonia, it becomes slightly turbid.

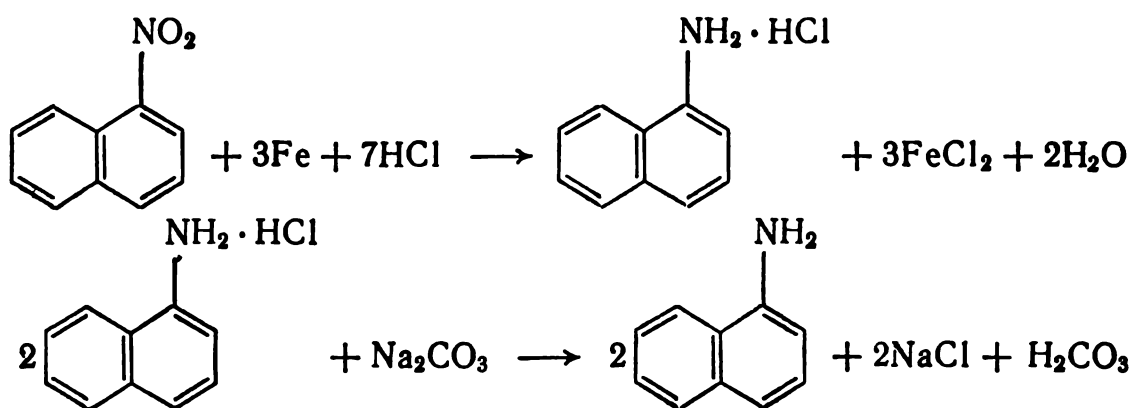
2. Unlike *o*-toluidine, it does not produce a colour when mixed with a dilute chlorinated lime solution.

α -NAPHTHYLAMINE

Formula:



Main reactions:



Reagents and Equipment

α -Nitronaphthalene . . .	13.8 g	Beaker, thick-walled (500 ml)	1
	(0.08 mole)	Stirrer	1
Iron (filings)	20 g	Funnel, dropping (100 ml)	1
	(0.36 gram atom)	Thermometer	1
Hydrochloric acid		Funnel, Büchner	1
(<i>d</i> = 1.19)	2 ml	Flask, Bunsen	1
Ethyl alcohol	50 ml	Apparatus, vacuum distilla-	1
Sodium carbonate		tion	1

Assembly

1. A 500-ml thick-walled beaker, immersed in a water bath, is fitted with a thermometer, a stirrer and a dropping funnel.
2. Suction apparatus (see Fig. 2.21).
3. Vacuum distillation apparatus (see Fig. 3.9).

Procedure

Twenty grams of iron filings are put in the 500-ml thick-walled beaker and a solution of 2 ml of concentrated hydrochloric acid in 75 ml of water, preliminarily heated to 50 °C, is added. A solution of 13.8 g of α -nitronaphthalene in 50 ml of ethyl alcohol is prepared. It is placed in the dropping funnel from which, throughout an hour, it is put in small portions into the thick-walled beaker while vigorously stirring the reaction mixture. In this case, the temperature of the mixture must be no higher than 75 °C. The reaction is considered complete when a sample completely dissolves in dilute hydrochloric acid.

1. To reduce α -nitronaphthalene, the iron filings must be minute, clean and degreased. To degrease them, they are washed with ether and dried in air.

2. α -Nitronaphthalene is insoluble in water, and therefore the reaction must be carried out in a water-alcoholic solution.

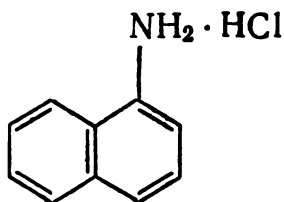
After the reaction, the mixture is heated for 15 min and then alkalinized with sodium carbonate until a weak-alkaline reaction occurs. To isolate the α -naphthylamine, the solution is diluted with water.

α -Naphthylamine does not dissolve in water, but partially dissolves in alcohol. Therefore, it can be isolated by diluting the alcohol in the reaction mixture with water.

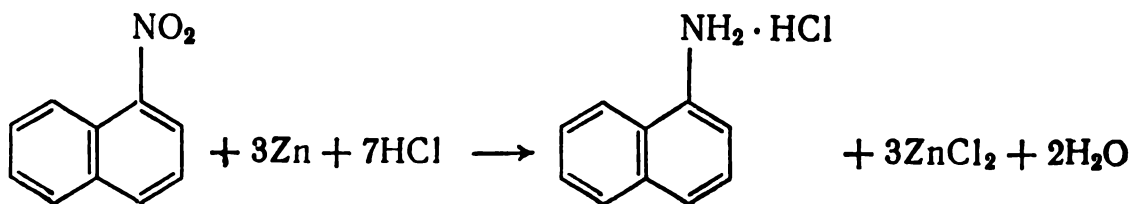
The α -naphthylamine isolated is sucked off, together with the remaining iron filings, in the Büchner funnel. The residue is dried in air and then distilled under vacuum. The α -naphthylamine yield is about ten grams.

PREPARATION OF α -NAPHTHYLAMINE HYDROCHLORIDE

Formula:



Main reaction:



Reagents and Equipment

α -Nitronaphthalene . . .	10.5 g (0.06 mole)	Flask, round-bottom (200 ml) . . .	1
Zinc, granulated	16 g (0.25 mole)	Funnel, Büchner	1
		Flask, Bunsen	1
Hydrochloric acid ($d = 1.19$)	45 ml (0.55 mole)	Thermometer	1
Ethyl alcohol	50 ml		

Assembly

A suction apparatus consisting of the Büchner funnel and the Bunsen flask (see Fig. 2.21).

Procedure

Fifty millilitres of ethyl alcohol and 10.5 g of α -nitronaphthalene are put in the 200-ml round-bottom flask. Afterwards, 45 ml of concentrated hydrochloric acid are added to the mixture and the flask is heated slightly in a water bath. Sixteen grams of granulated zinc are gradually added in small portions to the solution obtained. The temperature of the reaction mixture must be no higher than 75 °C.

After the reaction, the hot solution is passed through a fluted filter in a funnel for hot filtration (p. 53). The filtrate is cooled and the α -naphthylamine hydrochloride crystals which have precipitated are sucked off, washed with a small amount of alcohol and dried in air. The yield of α -naphthylamine hydrochloride is about eight grams.

α -Naphthylamine is a colourless, crystalline substance with an unpleasant odour. It darkens in air as a result of oxidation, dissolves sparingly in water and well in alcohol, acids and ether. Its molecular weight is 143.18; b.p., 301 °C; m. p., 50 °C, and d , 1.120.

α -Naphthylamine hydrochloride is a colourless substance with needle crystals. It dissolves in alcohol and ether, and dissolves but sparingly in cold water. α -Naphthylamine is widely used in dye synthesis and laboratory syntheses.

Characterization Test. 1. A pink colour appears when sulphanic acid and a drop of a sodium nitrite solution are added to an aqueous α -naphthylamine solution acidified with acetic acid.

2. Dark blue-green flakes separate when α -naphthylamine acidified with hydrochloric acid is heated together with ferric chloride.

Chapter 14

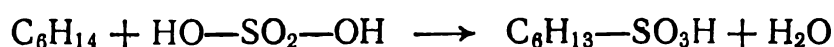
SULPHONATION REACTIONS

Sulphonation is the introduction of a sulpho group, $\text{—SO}_2\text{OH}$, into an organic compound. The reaction products are sulphonic acids (sulpho acids). Sulphonation is widely used in laboratories and industry.

Sulphonic acids and their derivatives are used in various ways; they are intermediate in the production of phenols and naphthols. Many derivatives of sulphonic acids are used for producing azo dyes, detergents, medicinals and surfactants, and are also employed as alkylating agents and disinfectants.

To introduce a sulpho group, use is made of various sulphonating agents: sulphuric acid of different concentrations, oleum, sulphur trioxide, sulphur dioxide and oxygen, sulphurous acid in the form of alkali salts, sulphur dioxide and chlorine, chlorosulphonic acid, etc.

Paraffin hydrocarbons are stable towards the action of ordinary sulphonating agents. Higher paraffins (from hexane) are sulphonated by 15 per cent oleum at the boiling point:



The sulphonation of paraffins and cycloparaffins by a mixture either of sulphur dioxide and chlorine (sulphochlorination), or of sulphur dioxide and oxygen (sulphoxidation), is of great industrial importance.

14.1. SULPHONATION OF AROMATIC COMPOUNDS

A characteristic feature which distinguishes the aromatic hydrocarbons from the paraffin ones is the readiness with which aromatic compounds are sulphonated by sulphuric acid.

Polycyclic aromatic hydrocarbons (anthracene, phenanthrene, etc.) are sulphonated most readily, naphthalene is sulphonated with greater difficulty, and benzene, with even greater difficulty.

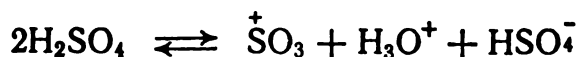
The sulphonation of sulphuric acid is a reversible process:



The water separated in the reaction reduces the concentration of sulphuric acid, which loses its sulphonating properties, and

causes a reversible reaction, i.e., the hydrolysis of the sulphonic acid being formed. In sulphonation, therefore, use is made of either a large excess of sulphuric acid (ranging from a two-fold to a five-fold volume) or oleum which has enough sulphuric anhydride for binding the water being separated.

A study of the kinetics of the sulphonation reaction has shown that the sulphonating agent is the sulphonium ion $\overset{+}{S}O_3$ which is formed according to the following reaction:



The readiness with which the derivatives of aromatic hydrocarbons are sulphonated depends also on the nature of their substituents. Substituents of the first kind, arranged in the order of their decreasing effect, i.e., $OH > OR > NH_2 > NHCOR > R$ (where R is an alkyl), facilitate the introduction of the sulpho group. *Meta*-directing substituents, i.e., $NO_2 > SO_3H > CO > COOH$, and halogens hinder the introduction of the sulpho group.

To obtain polysulphonic acids of the aromatic series, the compound being sulphonated is either treated immediately with the necessary amount of sulphuric acid or oleum, or sulphonation is carried out stepwise, selecting the best temperature and a suitable concentration for every "step". In this case, the conditions are more drastic than those when monosulphonic acids are being obtained.

An important factor which affects the sulphonation reaction is temperature. An elevation of temperature not only accelerates the process, but also promotes the formation of various by-products (polysulphonic acids, sulphones, and oxidation and condensation products). But this is not the only reason for strictly maintaining a definite optimum temperature for every sulphonation process. The temperature conditions often determine the site of entry of the sulpho group into the aromatic ring. When compounds with substituents of the first kind are being sulphonated, an elevation of temperature increases the *para*-isomer yield. At 0°C, for instance, *o*- and *p*-toluenesulphonic acids are formed in approximately equal amounts, while at 100°C, 79 per cent of the *para*-isomer and only 13 per cent of the *ortho*-isomer are obtained. When phenol is sulphonated at room temperature, *o*-phenolsulphonic acid is formed, and when it is sulphonated at 100°C, a *para*-isomer is formed.

The direction of naphthalene sulphonation also largely depends on temperature. When 100 per cent sulphuric acid is sulphonated at 80-90°C, mainly α -naphthalenesulphonic acid is obtained together with the β -isomer in the ratio of 96 : 4. When naphthalene is sulphonated at 160°C, mainly β -naphthalenesulphonic acid is obtained together with the α -isomer and the products of the further sulphonation of disulphonic acid. This is because, in naphthalene sulphonation, two reversible reactions occur with the formation of

α - and β -isomers:



At low temperatures, α -naphthalenesulphonic acid is formed several times faster than the β -isomer. Therefore, α -naphthalenesulphonic acid is mainly obtained together with an impurity of the β -isomer. At a higher temperature, α -naphthalenesulphonic acid is hydrolyzed 16 times faster than the β -isomer. Therefore, the amount of α -naphthalenesulphonic acid decreases, while that of the β -isomer increases. It follows that, at high temperature, the equilibrium of naphthalene sulphonation is shifted to the left for the α -isomer, and to the right for the β -isomer as more resistant to hydrolysis.

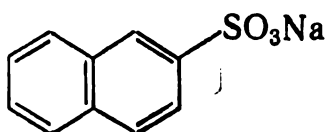
In some cases, the site of entry of the sulpho group depends on the catalyst. For instance, when anthraquinone is sulphonated without a catalyst, β -anthraquinonesulphonic acid is mainly formed, but when it is sulphonated in the presence of an insignificant amount of mercury salts, α -anthraquinonesulphonic acid is formed.

Sulphonic acids are substances which are difficult to describe because most of them have no definite melting and boiling points. Moreover, it is hard to get rid of inorganic impurities when free sulphonic acids are being isolated. Therefore, sulphonic acids are usually isolated in the form of salts which can be purified by crystallization. Many of these have characteristic melting points.

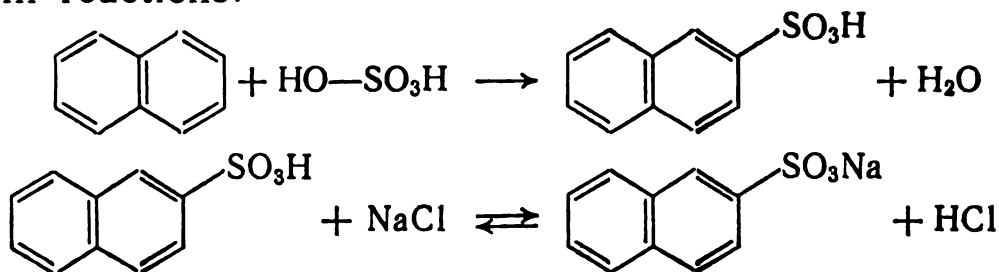
14.2. SYNTHESSES

β -NAPHTHALENESULPHONIC ACID (SODIUM SALT)

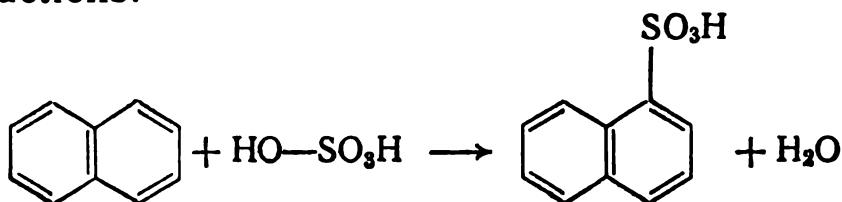
Formula:

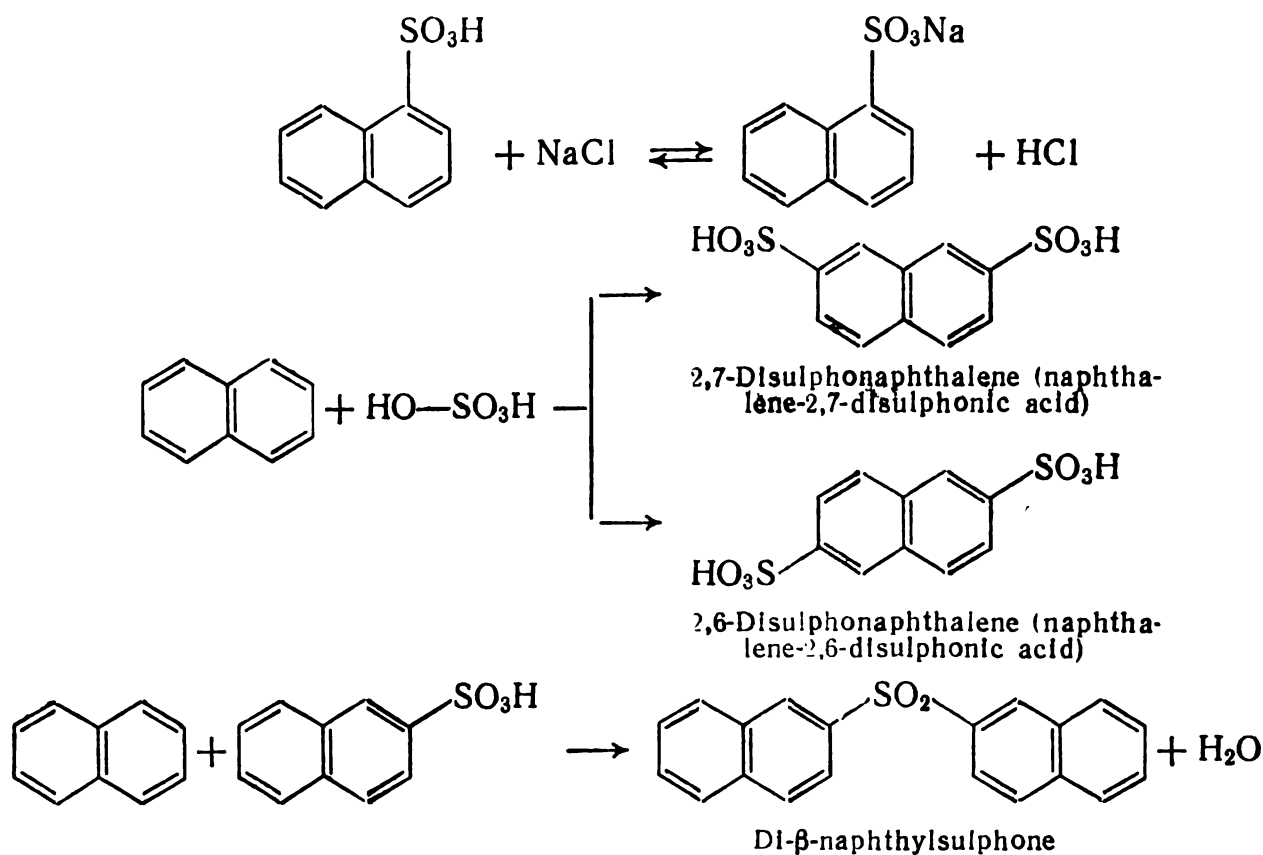


Main reactions:



Side reactions:





Reagents and Equipment

Naphthalene	12.8 g (0.1 mole)	Flask, round-bottom (100 ml)	1
Sulphuric acid ($d = 1.84$) . . .	12 ml (0.21 mole)	Beakers	2
Sodium chloride	38 g	Funnel, Büchner	1
Sodium bicarbonate	8 g	Flask, Bunsen	1
		Thermometer	1

Assembly

1. A thermometer is so inserted into the 100-ml round-bottom flask that its bulb is immersed in the reaction mass. The flask is then placed in a sand bath. The neck of the flask is closed with a stopper having a side slit.

2. Suction apparatus (see Fig. 2.21).

Procedure

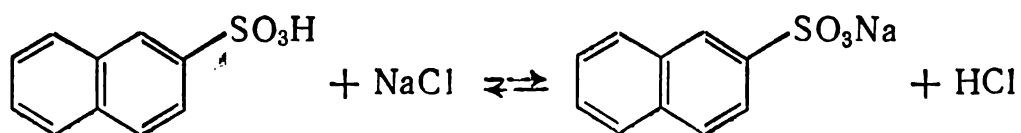
Twelve millilitres of concentrated sulphuric acid are poured into the round-bottom flask of apparatus 1 and portions of 12.8 g of thoroughly ground naphthalene are gradually added while stirring. When all the acid has been poured in, the reaction mass is heated at 160-170°C (the thermometer is in the flask) in a sand bath for four hours while making sure that the temperature does not rise. An elevation of temperature can cause side reactions, i.e., oxidation and the formation of polysulphonic acids and sulphones.

After the reaction, the mixture is slightly cooled and, while stirring, gradually poured into a beaker containing 200 ml of cold water. A precipitate consisting of unreacted naphthalene and a small amount of a by-product, i.e., di- β -naphthalenesulphone, is then formed. It is sucked off in the Büchner funnel or separated by decantation (the side reaction can be precluded by using a large excess of sulphuric acid).

The excess of initial sulphuric acid is neutralized by gradually adding eight grams of sodium carbonate. To obtain sodium β -naphthalenesulphonate, the sulpho mass is gradually poured (while stirring it with a wooden spatula) into a sodium chloride solution which is saturated in the cold and placed in an ice-cooled beaker (the saturated sodium chloride solution is prepared by dissolving 38 g of NaCl in 125 ml of hot water).

Anhydrous β -naphthalenesulphonic acid is highly hygroscopic. When it combines with water, it swells and crystallizes with three water molecules. Therefore, it is isolated as sodium salt, which is a stable compound that can be processed further.

β -Naphthalenesulphonic acid is a strong acid and easily drives out hydrochloric acid from a sodium chloride solution:



To thoroughly separate sodium salt, the β -naphthalenesulphonic acid mass is allowed to stand in ice for 30 min.

The precipitated sodium β -naphthalenesulphonate, together with the sodium α -naphthalenesulphonate impurities, is filtered off in the Büchner funnel and washed with a small amount of water. The salt is dried in a drier at 100 °C.

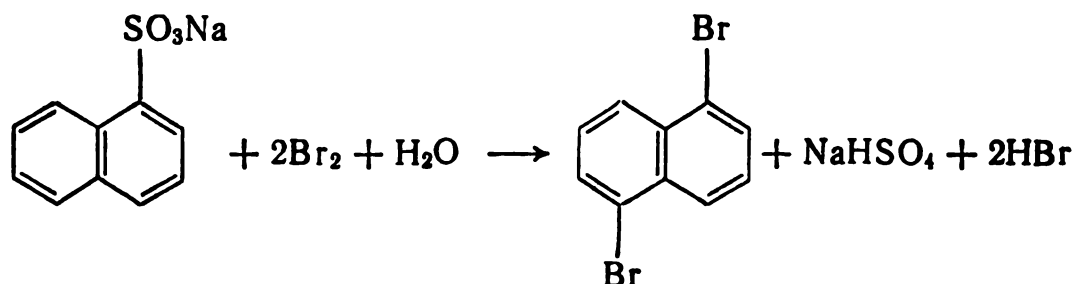
To cleanse sodium β -naphthalenesulphonate from sodium chloride, it should be recrystallized from absolute ethyl alcohol. The yield of crude sodium β -naphthalenesulphonate is about 15 g.

The foregoing method is used for obtaining sodium β -naphthalenesulphonate with a small amount of impurities of the sodium salt of the α -isomer. The α -isomer impurities are separated on the basis of the different solubilities of the calcium salts of both acids in water. β -Naphthalenesulphonate is less soluble, and therefore it is the first to precipitate.

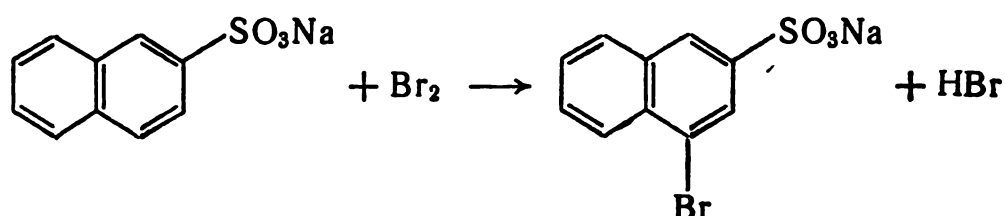
Sodium β -naphthalenesulphonate is obtained in the form of minute, glassy flakes. In a mixture containing the α -isomer, it crystallizes in the form of very fine, lustrous flakes. The mixture of both isomers dissolves well in water.

The presence of the α -isomer impurity in crude salt is detected in the following way: the crude β -naphthalenesulphonate is heated together with bromine water. Under the action of bromine, sodium α -naphthalenesulphonate be-

comes 1,5-dibromonaphthalene, which is separated as white turbidity,



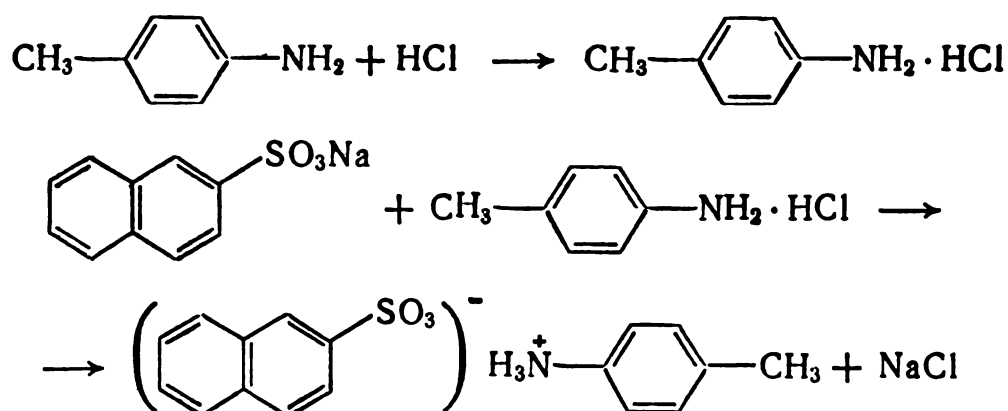
Sodium β -naphthalenesulphonate is not replaced by bromine, while the 4-bromonaphthalene-2-sulphonic acid formed is soluble in water:



Anhydrous β -naphthalenesulphonic acid melts at 91°C . Its monohydrate melts at 124°C , and its crystal hydrate, at 83°C .

β -Naphthalenesulphonic acid is used for obtaining β -naphthol and H-acid. It is an intermediate in dye synthesis. Moreover, β -naphthalenesulphonic acid forms various functional derivatives (ethers, acid chlorides, amides), which are used for identification.

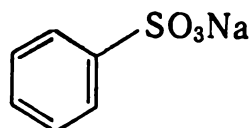
Characterization Test. To identify β -naphthalenesulphonic acid, it is necessary to use its sodium salt together with *p*-toluidine. To this end, one gram of the sodium salt obtained is dissolved in a small amount of boiling water and 0.5 ml of *p*-toluidine is added. When the solution becomes clear, 2 ml of concentrated hydrochloric acid are added. The test tube containing the solution is cooled in ice and the salts of *p*-toluidine and β -naphthalenesulphonic acid formed (m.p. $217\text{--}218^\circ\text{C}$) are crystallized by rubbing the test tube side with a rod:



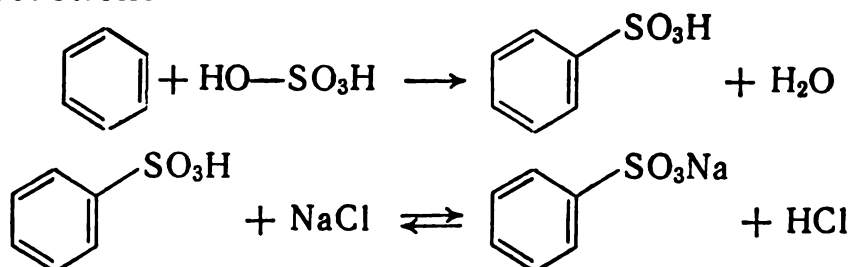
The crystals obtained are sucked off in a small funnel, washed with water and recrystallized from hot water or diluted ethyl alcohol.

BENZENESULPHONIC ACID (SODIUM SALT)

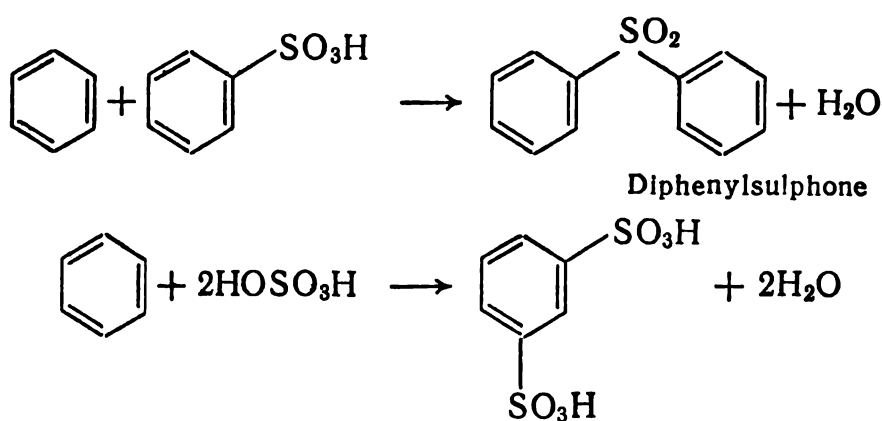
Formula:



Main reactions:



Side reactions:

*m*-Disulphobenzene (benzene-*m*-disulphonic acid)**Reagents and Equipment**

Benzene	5 ml	Flask (50 ml)	1
	(0.05 mole)	Beaker (100 ml)	1
Sulphuric acid, monohydrate	10 ml	Flask, Bunsen	1
Sodium chloride	10 g	Funnel, Büchner	1

Procedure

Work must be done *in a fume cupboard!* A saturated solution of pure sodium chloride (10 g of NaCl in 35-40 ml of water) is prepared in a beaker and cooled with icy water.

Ten millilitres of sulphuric acid (monohydrate) are poured into a flask and 5 ml of benzene are carefully added in small portions, shaking the flask after every addition. A new portion is added when the former has dissolved. If the reaction occurs too rapidly, the flask must be cooled from the outside with icy water. When all the benzene added has dissolved and the solution has cooled, the mixture is added in small portions to the saturated cold solution of sodium chloride.

Somewhat later, sodium benzenesulphonate precipitates in the form of lustrous flakes, especially when the side of the beaker is

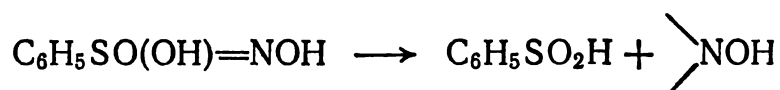
slightly rubbed with a glass rod and the mixture is cooled. The flakes are sucked off in the Büchner funnel and washed with a small amount of a saturated sodium chloride solution. Sodium benzenesulphonate is dried at first in air and then in a drier at 110 °C. The sodium benzenesulphonate yield is 8-9 g.

Sodium benzenesulphonate contains the sodium chloride impurity. It can be purified by recrystallizing it from alcohol.

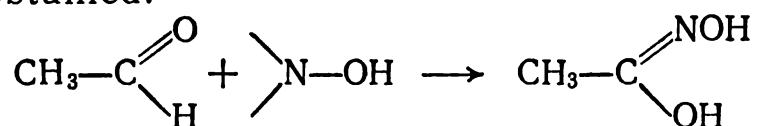
Benzenesulphonic acid consists of colourless crystalline plates whose molecular weight is 158.18. Anhydrous acid melts at 171-172 °C. Its monohydrate melts at 45-60 °C, and its crystal hydrate, at 43-44 °C. Benzenesulphonic acid dissolves well in water and alcohol, and poorly in benzene.

It is used for producing phenol and benzonitrile, and as a catalyst in some condensation and polymerization reactions.

Characterization Test. Small amounts of benzenesulphonic acid and thionyl chloride (SOCl_2) are mixed together and the benzene sulphochloride formed is evaporated to dryness in a micro crucible. When benzene sulphochloride is treated with four drops of an alcoholic solution of hydroxylamine, benzenesulphohydroxamic acid, $[\text{C}_6\text{H}_5\text{SO}(\text{OH})=\text{NOH}]$, is formed. It is then alkalized with a 5 per cent sodium carbonate solution. Soda decomposes benzenesulphohydroxamic acid to benzenesulphonic acid and the nitroxyl residue:



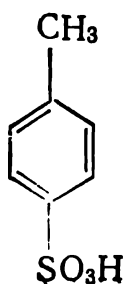
Then, two drops of acetaldehyde are added and acetohydroxamic acid is obtained:



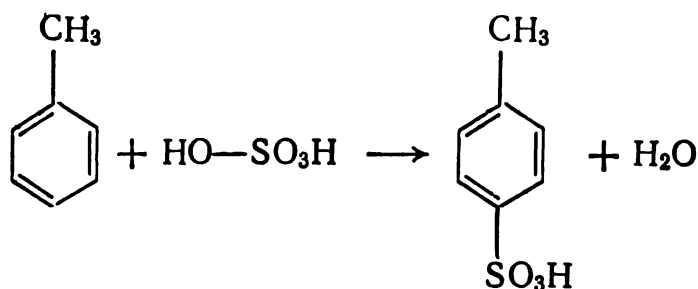
When the solution cools, it is neutralized with hydrochloric acid, and then two drops of a dilute aqueous solution of ferric chloride are added. In this case, the solution becomes red, i.e., hydroxamic acids give strongly coloured iron complexes when they interact with ferric chloride, FeCl_3 .

p-TOLUENESULPHONIC ACID

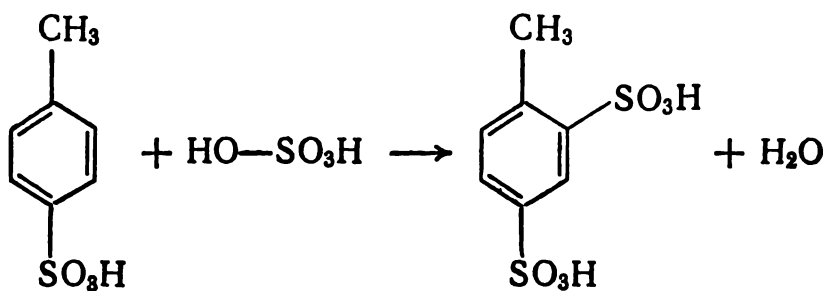
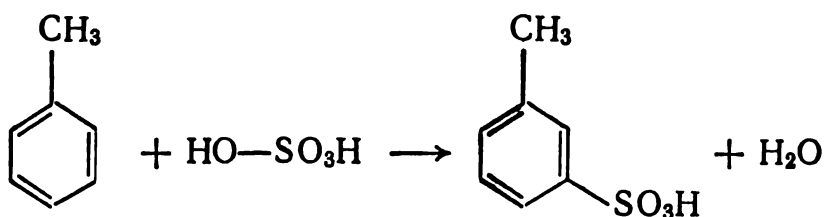
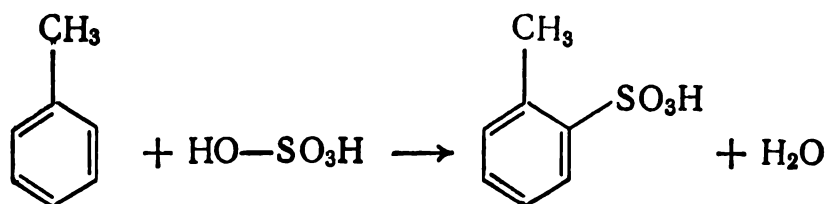
Formula:



Main reaction:

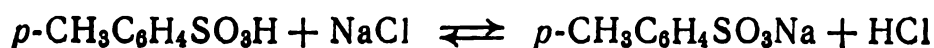


Side reactions:



Toluene sulphonates very easily because the methyl group is an *ortho*, *para*-directing substituent and facilitates the introduction of the sulpho group, mainly in the *ortho*- and *para*-positions.

Preparation of Sodium Toluenesulphonate



Reagents and Equipment

Toluene	16 ml (0.15 mole)	Flask, round-bottom, long-necked (100 ml)	1
Sulphuric acid ($d = 1.84$)	9.5 ml (0.18 mole)	Condenser, reflux	1
Sodium carbonate . . .	8 g	Beaker	1
Sodium chloride	20 g	Funnel, Büchner	1
		Flask, Bunsen	1

Assembly

1. A few boiling stones are put in the 100-ml long-necked, round-bottom flask, which is fitted with a reflux condenser.
2. Suction apparatus (see Fig. 2.21).

Procedure

Sixteen millilitres of toluene are put in the round-bottom flask of apparatus 1 and 9.5 ml of concentrated sulphuric acid are added carefully. The reaction liquid is boiled slightly for one hour on an asbestos gauze while shaking the flask from time to time (when mixing the layers).

Toluene will boil uniformly when it is heated properly. Excessive heating causes toluene to be driven out of the reaction region and promotes the formation of disulpho derivatives. Continuous shaking accelerates the reaction and makes it possible to obtain a high yield.

The reaction is considered complete when the toluene layer almost disappears and the condensate occasionally drips from the condenser. The warm reaction mixture is then poured into a beaker containing 70 ml of water (the mixture must be heated if it begins to crystallize) and the flask is rinsed from a wash bottle. The acid solution is carefully neutralized with eight grams of sodium carbonate, which are introduced in small portions. Then 20 g of sodium chloride are added to the solution and the mixture is heated until it boils (if sodium chloride does not dissolve, add some more water). The solution is cooled with iced water.

The sodium toluenesulphonate crystals which have precipitated are sucked off in the Büchner funnel and squeezed between sheets of filter paper.

The yield of sodium toluenesulphonate with the sodium chloride impurity is about eight grams.

*Preparation of Free *p*-Toluenesulphonic Acid*

To obtain crystalline *p*-toluenesulphonic acid, an excess of toluene is heated together with concentrated sulphuric acid ($d = 1.84$). In this case, the water which separates during the reaction is removed from the reaction mixture. As a result, the reaction occurs almost to the end and the amount of *p*-toluenesulphonic acid increases to 85 per cent.

Assembly

1. A round-bottom flask fitted with a reflux condenser and an attachment for separating water.
2. A suction apparatus having a funnel with a glass filter.

Procedure

Forty-five millilitres of toluene and 8 ml of concentrated sulphuric acid are put in the round-bottom flask of apparatus 1 and the mixture is so boiled for five hours that toluene vapours reach the condenser. The water which separates in the reaction is condensed in the reflux condenser and drips into attachment. After five hours of boiling, about 3.5 ml of water are collected. The amount of water which separates is somewhat greater than that calculated due to the moisture of the reagents used.

After heating, the reaction mass is allowed to cool and 2.5 ml of water are added to it. In this case, toluenesulphonic acid crystallizes out as a hydrate. Unreacted toluene is decanted, and then the crystals are sucked off in the funnel having a glass filter and wrung well with a glass stopper. In this case, *o*-toluenesulphonic acid, which is formed as a by-product, remains in the filtrate.

For purification purposes, the hydrate of *p*-toluenesulphonic acid is dissolved in a small amount of hot water (20 ml), and then a triple amount of concentrated hydrochloric acid is added to the solution. The solution is cooled in icy water, and the crystals which have precipitated are sucked off in the funnel having a glass filter and washed with a small amount of cold concentrated hydrochloric acid. This purification process is repeated twice. The hydrate of *p*-toluenesulphonic acid is then dried in a desiccator over solid sodium hydroxide until the reaction with hydrochloric acid is negative (HCl with AgNO_3 forms AgCl turbidity). The *p*-toluenesulphonic acid yield is about eight grams.

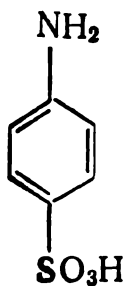
p-Toluenesulphonic acid crystallizes with one water molecule ($p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$). The crystals are colourless prisms which melt at $104\text{--}105^\circ\text{C}$. At 150°C , they are hydrolyzed.

p-Toluenesulphonic acid is used for obtaining *p*-cresols and for titrating amines.

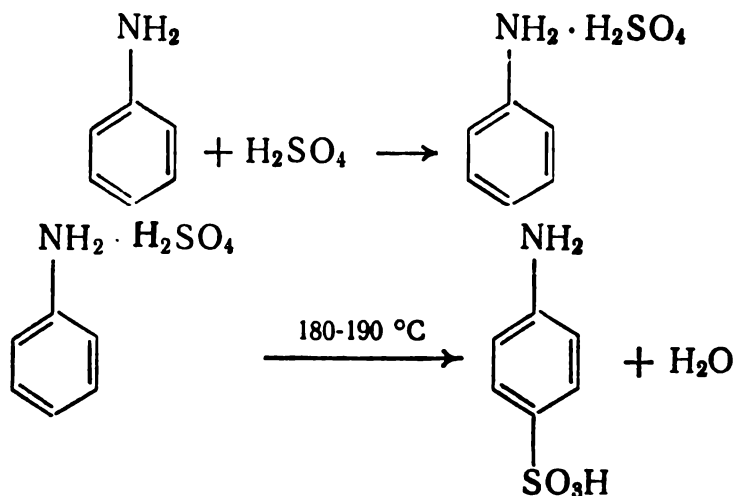
To identify *p*-toluenesulphonic acid, its salt is obtained together with *p*-toluidine, melts at 197°C (for preparation of the appropriate salt of β -naphthalenesulphonic acid, see p. 252).

SULPHANILIC ACID

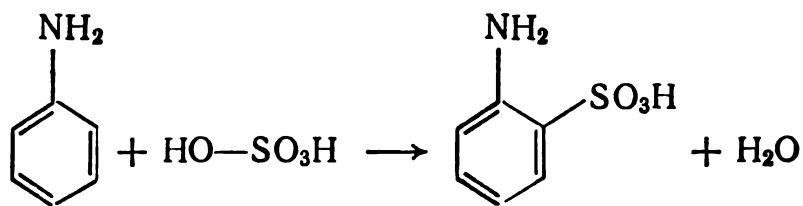
Formula:



Main reactions:



Side reaction:



To obtain sulphanilic acid and other monosulphonic acids of primary aromatic amines, use is generally made of the method in which bisulphates of many primary amines are converted into sulphonamic acids, mainly in the *para*-position, when they are heated for several hours at 180-190 °C. Aniline readily sulphonates. In this case, the by-product formed is orthanilic acid (*o*-aminobenzenesulphonic acid) which can be obtained with a high yield by sulphonating aniline with chlorosulphonic acid in organic solvents.

Reagents and Equipment

Aniline, freshly distilled . . .	9.3 g or 9 ml	Mortar, porcelain	1
	(0.1 mole)	Dish, porcelain	1
Sulphuric acid ($d = 1.84$) . . .	16.3 ml	Flask, Bunsen	1
	(0.3 mole)	Funnel, Büchner	1
Sodium hydroxide	4 g	Thermometer	1
Hydrochloric acid, 2 <i>N</i> solution			
Activated charcoal			

Procedure

Work must be done *in a fume cupboard!* **Variant 1.** Concentrated sulphuric acid in an amount of 5.5 ml is put in a porcelain mortar and 9.3 g of freshly distilled aniline are added gradually in small portions. The aniline bisulphate formed is then thoroughly ground with a pestle and transferred to a porcelain dish. The dish is covered with a piece of asbestos cardboard and a thermometer is put in the aniline salt through a hole in the cardboard. Dry solid

sulphanilic acid is formed when the aniline salt is heated in an air bath for three or four hours at 175-180 °C. The reaction is considered complete when a sample of the sulpho mass, diluted with an alkaline solution, no longer forms aniline drops.

After the reaction, the hot sulphanilic acid is ground in a mortar and, to purify it, is dissolved in a solution of 4 g of sodium hydroxide in 40 ml of water. Next, the solution is boiled for five minutes with activated charcoal to decolorize it. It is then filtered off and sulphanilic acid is separated, acidifying it with hydrochloric acid until an acid reaction occurs (the congo red test is used). The solution is cooled with cold water and, in 20 min, the crystals of sulphanilic acid which have precipitated are sucked off in the Büchner funnel (see Fig. 2.21). The crystal hydrate of sulphanilic acid ($p\text{-H}_2\text{NC}_6\text{H}_4\text{SO}_3\text{H}\cdot 2\text{H}_2\text{O}$) is then recrystallized from water and dried. The sulphanilic acid yield is about 11 g.

Variant 2. Put 9.3 g of aniline in the 100-ml round-bottom flask and gradually add 16.3 ml of concentrated sulphuric acid while continuously shaking the flask. The mixture is heated in an oil bath at 180-190 °C *in a fume cupboard* until the water-diluted sample no longer separates aniline (3-4 h) when a sodium hydroxide solution is added.

Aniline sulphate dissolves in alkali. If the reaction has not completed, free aniline separates from aniline sulphate and causes turbidity owing to its poor solubility.

The cooled reaction mixture is poured (while stirring) into a beaker containing a small amount of cold water. The crystals of sulphanilic acid which have precipitated are then filtered off and washed with a small amount of water. The acid is recrystallized from hot water (when need be, activated charcoal is used). The yield of sulphanilic acid is about 10 grams.

Sulphanilic acid (p -aminobenzenesulphonic acid) is a colourless, crystalline substance. Its molecular weight is 173.18, and it decomposes at 280-300 °C. A dihydrate with a molecular weight of 209 crystallizes out of an aqueous solution at 0-21 °C, and a monohydrate crystallizes out at 21-40 °C. Anhydrous sulphanilic acid crystallizes out at a higher temperature.

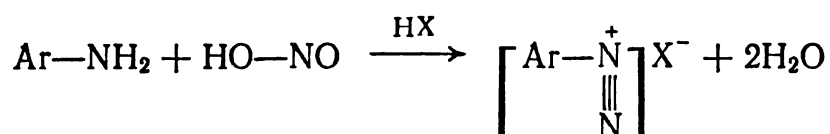
It is used in industry for producing azo dyes, and in laboratories for determining nitriles and detecting osmium, ruthenium, etc. Amides of sulphanilic acid are used for producing medicinals.

Characterization Test. When sulphanilic acid is treated with bromine water in a hot aqueous solution, it turns into tribrom-aniline which precipitates as fine crystals.

Chapter 15

DIAZOTIZATION AND AZO COUPLING REACTIONS

The diazotization reaction, discovered by Griess in 1858, consists in the formation of diazonium salts when primary aromatic amines interact with nitrous acid in an acid medium:

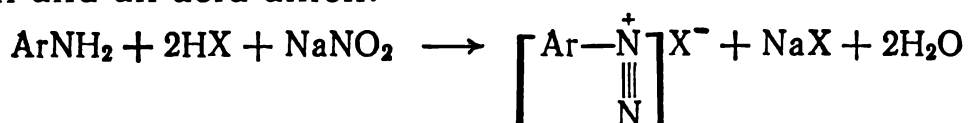


where Ar = aromatic radicals;

X = anion of a mineral acid.

This reaction is very characteristic of primary aromatic amines. It is very important industrially and is widely used in laboratories. The reaction is important in laboratory practice because it can be used for carrying out many syntheses and distinguishing primary amines of the fatty series from primary aromatic amines. In industry, the diazotization reaction is used for synthesizing intermediates, dyes and pharmaceuticals.

To carry out the diazotization reaction, it is necessary to use not free nitrous acid, which is very unstable, but an acid which separates when sodium or potassium nitrite interacts with a mineral acid (in most cases, hydrochloric or sulphuric acid). In this case, a diazonium salt is formed, and it dissociates into the diazonium ion and an acid anion:



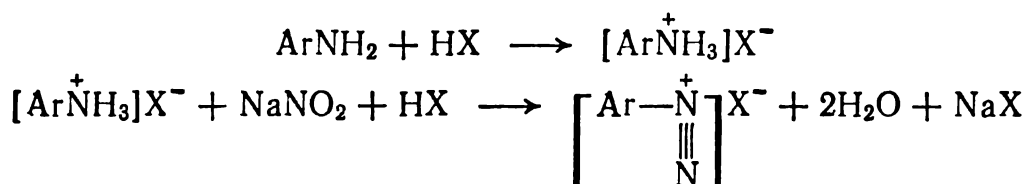
The diazotization reaction rate depends on the amine structure and the nature of the anion which participates in the acid reaction.

Amines which have *meta*-directing substituents ($-\text{NO}_2$, $-\text{SO}_3\text{H}$, $-\text{COOH}$, etc.) in the aromatic ring are diazotized more rapidly than those which have *ortho*, *para*-directing substituents ($-\text{CH}_3$, $-\text{OH}$, $-\text{OCH}_3$, etc.). *Meta*-directing substituents reduce the basicity of an amino group. The salts of such amines are readily hydrolyzed with water (e.g., nitroanilines). Therefore, ordinary conditions of diazotization in an aqueous medium are unsuitable in this case. The diazotization reaction is carried out by solid sodium nitrite in a concentrated sulphuric acid medium.

Special conditions must be created for diazotizing two amino groups in a single benzene ring. Three amino groups cannot be diazotized because only resinification products are formed.

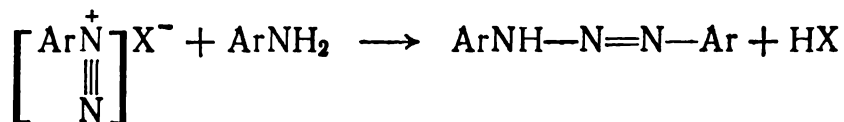
To obtain diazonium salts, the amino derivatives of benzene, naphthalene, anthraquinone, and aminobenzene- and aminonaphthalenesulphonic acids are used in most cases.

To diazotize 1 mole of aromatic amine, it is theoretically necessary to use 1 mole of sodium nitrite and 2 moles of a monobasic mineral acid. In this case, 1 mole of the acid is used for forming an aromatic amine salt, and 1 mole, for forming nitrous acid *:

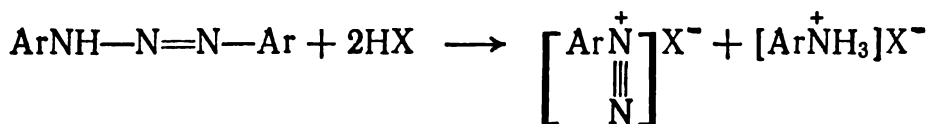


In practice, a considerably greater amount of the acid is used. For amines of the aniline type, it is necessary to use 2.5-3 moles of a mineral acid per mole of an amine and per mole of sodium nitrite. The acid concentration must be higher for amines which are more weakly basic.

Excess mineral acid is needed for precluding the combination of the diazonium salt formed with the free amine which has not reacted yet. For instance, in a weakly acidic medium, the side reaction between a diazonium salt and a primary amine occurs readily with the formation of diazoamino compounds:



But under the action of excess mineral acid, the diazoamino compound decomposes into a diazonium salt and an amine salt:



The diazotization reaction is carried out in a thick-walled beaker while continuously stirring the reaction mixture so as to preclude local superheatings.

Diazonium salts are very unstable and, when the temperature is elevated, are readily decomposed by water. Therefore, the diazotization reaction should be carried out at low temperatures (0-5 °C). To this end, the beaker is cooled from the outside by ice and, if need be, pieces of ice may be added to the reaction mass.

Nitrous acid interacts gradually with amine because this reaction is not an ionic one. Therefore, sodium nitrite should be added gradually (dropwise) so as to prevent free nitrous acid from accumulating.

* It has been ascertained that free amine, and not its salt, undergoes diazotization.

Diazotization should be so carried out that brown vapours of nitrogen oxides will not be formed over the solution surface due to the preservation of excess amine salt in the reaction mixture when nitrous acid decomposes with the formation of nitrogen oxides. This salt may bind the diazo compound.

Diazotization is usually controlled by checking whether free nitrous and other mineral acids are present. To this end, drops of the reaction solution are deposited on iodized starch paper* and congo paper. The congo paper turns dark blue in the presence of strong mineral acids. The iodized starch paper turns dark blue under the action of the free iodine which is separated as a result of the interaction between potassium iodide and nitrous acid.

If diazotization occurs normally, iodized starch paper turns grey-dark blue, while congo paper, blue. When there is an excess of nitrous acid, a dark-brown spot appears on iodized starch paper. If there is not enough nitrous acid at the end of the reaction, sodium nitrite is added until a stable, but not an intense, colour appears on iodized starch paper.

If a coloured precipitate of a diazoamino compound separates during diazotization, it can be decomposed by adding a mineral acid.

Diazonium salt solutions cannot be allowed to stand for a long time and cannot be kept in the sunlight.

Attempts to separate diazonium salts from aqueous solutions usually fail. They can be isolated in a solid state only by carrying out the reaction in an alcoholic solution. Dry diazonium salts, however, are very dangerous because they explode when heated or hit. Therefore, reactions involving diazonium salts are always carried out in their aqueous solutions immediately after they are formed.

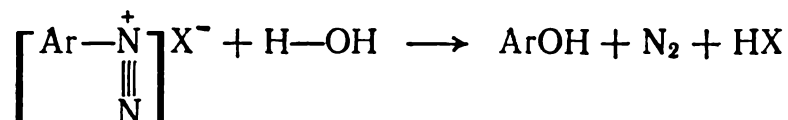
Diazonium salts are very reactive. They have two characteristic types of reactions: (1) reactions with the loss of nitrogen, and (2) reactions without the loss of nitrogen, including reduction reactions as a result of which aromatic hydrazines are formed.

15.1. DIAZONIUM SALT REACTIONS WITH LOSS OF NITROGEN

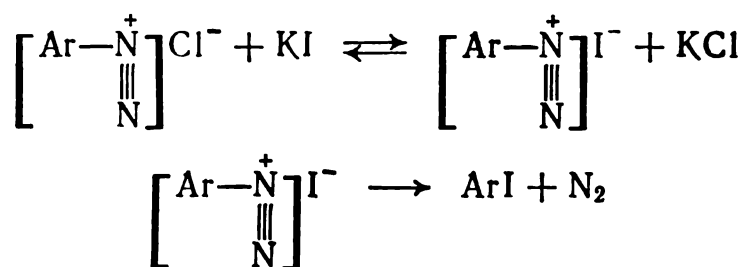
Most aromatic diazo compounds are unstable, readily decomposing substances. If the decomposition reaction is to be carried out under definite conditions, a diazonium group can be replaced by many other groups (OH, CN, Cl, Br, I, etc.).

* Iodized starch paper is filter paper impregnated with a solution of potassium iodide and starch paste, and then dried.

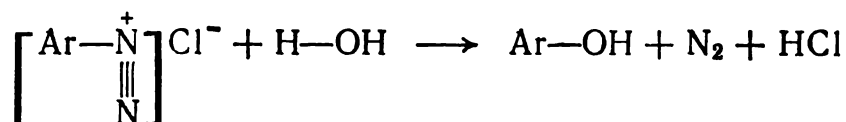
When diazonium salts are heated in aqueous acid solutions, a reaction occurs in which a diazonium group is replaced by a hydroxyl group, accompanied by a vigorous loss of nitrogen and the formation of phenols:



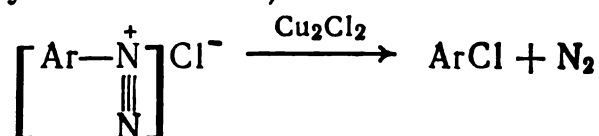
A diazonium group is replaced by iodine when a diazonium salt solution is heated together with a potassium iodide solution:



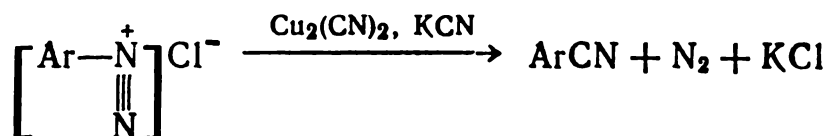
Phenol is obtained as a by-product of the reaction:



The presence of excess potassium iodide hinders the side reaction. A diazonium group cannot be replaced similarly by bromine or chlorine because these reactions give low yields. The yields can be increased by using cuprous chloride or copper powder as a catalyst (Sandmeyer's reaction):



The action of cyanides is not enough for replacing a diazonium group by a nitrile group. The reaction gives high yields only in the presence of cuprous cyanide or copper powder:

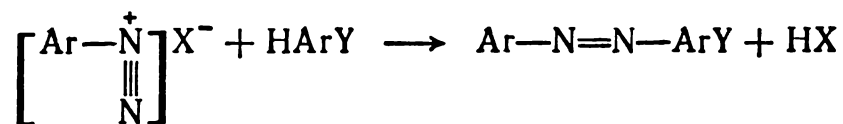


Sodium or potassium cyanides are used for this reaction. They are needed for forming the soluble complex salt $\text{Na}_3[\text{Cu}(\text{CN})_4]$.

15.2. DIAZONIUM SALT REACTIONS WITHOUT LOSS OF NITROGEN

The most important reactions of this group are the azo coupling reactions, i.e., the interaction between diazonium salts and aromatic amines or phenols that results in the formation of the compounds

$\text{Ar}-\text{N}=\text{N}-\text{Ar}$ according to the following general scheme:



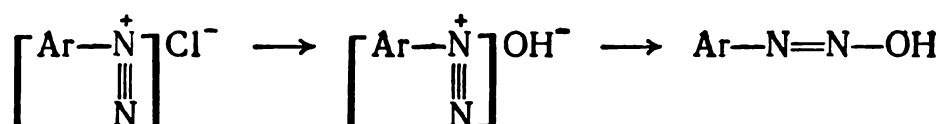
where X = acid anion;

$\text{Y} = -\text{NH}_2, -\text{NHAr}, -\text{NHAIK}, -\text{N}(\text{AIK})_2, -\text{OH}, -\text{OAIK}$
(such groups in dyes are called auxochromes).

The products of the azo coupling reactions, i.e., azo compounds, are very stable and are usually brightly coloured. Their colour is due to the presence of a chromophore in the molecule. The chromophore in this case is the azo group $-\text{N}=\text{N}-$, which is attached to two aromatic rings. But not all coloured substances are dyes. A dye, besides possessing colour properties, must be able to fix itself easily on various fabrics. Auxochromes enable it to do so.

The azo coupling reaction is widely used in technological processes for obtaining azo dyes.

Every azo coupling reaction has a definite optimum pH value. In a strongly acidic medium, a reaction as a rule occurs neither with aromatic amines nor with phenols due to the very low concentrations of free amine (owing to the formation of diazonium salts) and the phenolate ion (phenol dissociation is strongly suppressed). In a strongly alkaline medium, a free base, i.e., diazohydroxide, separates from a diazonium salt, and then rearranges itself into diazohydrate:



Diazohydrate is a weak acid, and, in an alkaline medium, it forms the salt $\text{Ar}-\text{N}=\text{N}-\text{ONa}$, which is incapable of azo coupling.

Therefore, a weakly acidic medium is the most favourable medium for azo coupling when amines are used, and a weakly alkaline medium is the most favourable one when phenols are used.

The shade of azo dyes greatly changes in conformity with the degree of acidity or alkalinity of a medium. For instance, helianthin in an alkaline medium is yellow; in a neutral medium, it is orange, and in an acid medium, reddish-pink. The colour of congo red is red in an alkaline medium and dark blue in an acid medium.

Amines which form diazonium salts are usually called diazo components of a dye, while amines and phenols which enter azo coupling are called azo components.

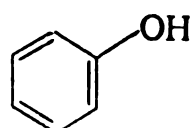
If the *para*-position in an azo component is free with respect to an amino or hydroxy group, azo coupling occurs in this position. If there are substituents in the *para*-position in this com-

ponent, azo coupling occurs in the *ortho*-position with respect to the amino or hydroxy group. The extent of easiness with which azo coupling occurs is determined by the nature of the reactants: it occurs easily with phenols, and with somewhat greater difficulty with amines. The activity of diazo components is enhanced by halogens and the carboxyl, carbonyl, nitro and sulpho groups. These substituents reduce the activity of azo components. Therefore, in selecting reaction conditions, the reactivity of diazo and azo components must be taken into account.

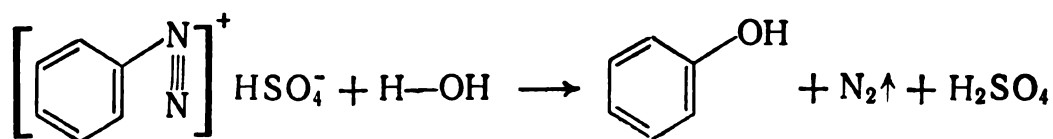
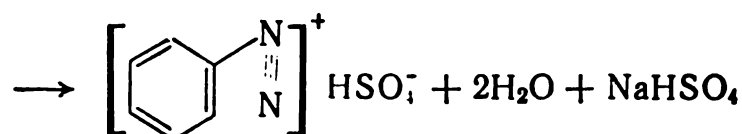
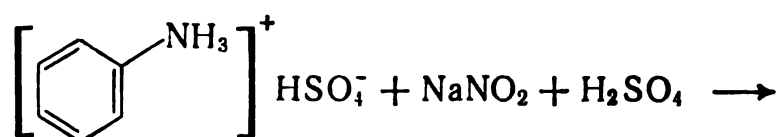
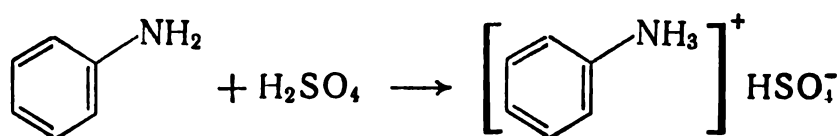
15.3. SYNTHESSES

PHENOL

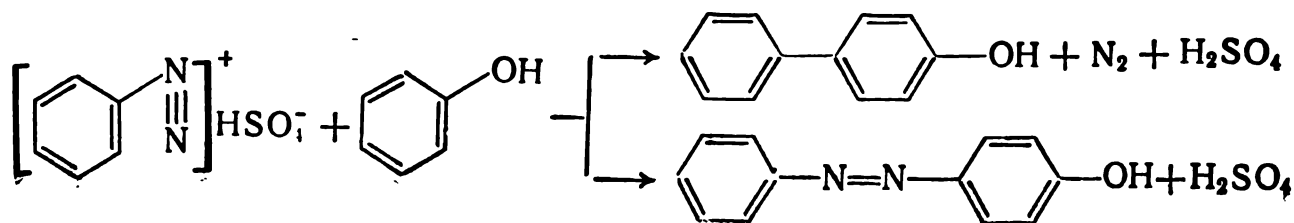
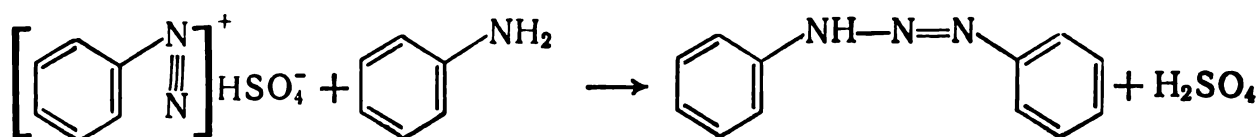
Formula:



Main reactions:



Side reactions:



Reagents and Equipment

Aniline	9.3 g or 9 ml (0.1 mole)	Beaker, thick-walled (300 ml)	1
Sulphuric acid ($d = 1.84$) .	10 ml (0.18 mole)	Flask, round-bottom (500 ml)	1
Sodium nitrite	7.25 g (0.11 mole)	Thermometers	2
Sodium chloride	7.5 g	Flasks, Würtz (150 ml) . .	2
Ether	60 ml	Funnel, dropping	1
Sodium sulphate	7 g	Funnel, separatory	1
Ice		Apparatus, steam distillation	1
		Condenser, Liebig	1
		Condenser, air	1
		Receivers	2

Assembly

1. A dropping funnel is lowered into a 300-ml thick-walled beaker which is in a bath with crushed ice. To prevent some nitrous acid from being lost as a result of its decomposition on the liquid surface with nitrogen oxides evolution, the end of the funnel must be immersed in the liquid by 1-2 cm.

2. A 500-ml round-bottom flask is connected to a reflux air condenser and put into a water bath in which a thermometer is placed.

3. Steam distillation apparatus (see Fig. 3.6).

4. A 150-ml Würtz flask, placed in a water bath, is connected to a thermometer and a Liebig condenser which has a bent adapter, whose end is lowered into a receiver.

5. A 150-ml Würtz flask is connected to a thermometer and an air condenser, under the other end of which a receiver is placed.

Procedure

Fifty millilitres of water are poured into the 300-ml thick-walled beaker and 10 ml of concentrated sulphuric acid are added while stirring.

The diazotization reaction rate is less in the sulphuric acid medium than it is in the hydrochloric acid medium. In the latter case, however, chlorine derivatives are formed as by-products.

Nine millilitres of freshly distilled aniline are slowly added to the hot solution while stirring. In this case, aniline should dissolve completely. If the solution is not clear, it should be heated until aniline has completely dissolved.

The solution obtained is cooled to room temperature. Then 75 g of finely crushed ice are gradually added, reducing the solution temperature to 0°C. While the ice is being added, the contents of the beaker must be vigorously stirred so that the aniline sulphate being partially separated is finely crystalline. Only then will it dissolve during diazotization.

A solution of 7.25 g of sodium nitrite in 30 ml of water, cooled to 0-5 °C, is slowly added to the cooled mixture from a dropping funnel while intensively stirring. During diazotization, the temperature of the reaction mixture should not rise above 8 °C. If need be, pieces of ice should be added to the mixture. When a larger part of the sodium nitrite solution has been added, the stopcock of the dropping funnel is closed, the mixture is stirred for another five minutes, and then a sample is taken to see whether free nitrous acid is present. If a dark spot is not formed when a drop of the liquid is deposited on iodized starch paper, indicating that nitrous acid has already completely entered into the reaction, another portion of the sodium nitrite solution may be added. If a dark spot is immediately formed on the paper, i.e., if nitrous acid is still not completely used up for diazotization, it is necessary to wait a few minutes more and then take another sample to see whether there is free nitrous acid. At the same time, make sure that the solution has an acid reaction (congo paper test) and, if need be, several drops of concentrated sulphuric acid should be added.

Diazotization can be considered complete if free nitrous acid is detected a few minutes after the last portion of sodium nitrite solution has been added to the reaction mixture. The reaction becomes retarded before the end of diazotization because the reagent concentration decreases. Therefore, a few minutes should pass before taking a sample. Besides the presence of free nitrous acid, the complete passage of aniline sulphate into solution also indicates the end of the reaction.

The clear diazonium salt solution obtained is transferred to the 500-ml round-bottom flask and allowed to stand for 15-20 min at room temperature. The phenyldiazonium sulphate in the aqueous solution gradually decomposes with the liberation of nitrogen and the formation of phenol. Next, to accelerate decomposition, the solution is heated in a water bath (apparatus 2) at 40-50 °C, shaking the contents of the flask from time to time until nitrogen bubbles no longer appear (15-20 min).

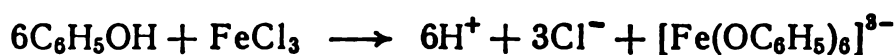
The phenol formed is then steam distilled (apparatus 3) until the distillate sample produces only faint turbidity with bromine water as a result of the formation of tribromophenol. Afterwards, 7.5 g of sodium chloride are added to the distillate and the flask is shaken until it dissolves almost completely. Phenol is then extracted from the distillate by ether (twice, using 30 ml every time) in a separatory funnel. The combined ethereal extracts are collected in a flask, dried over anhydrous sodium or magnesium sulphate (or over calcium chloride), and the ether is distilled in a water bath with a water condenser (apparatus 4). Phenol is distilled by heating the flask (apparatus 5) on an asbestos gauze, and the fraction which boils at 179-183 °C is collected. Phenol can be purified by

vacuum distillation. Phenol crystallizes when it cools. Its yield is about six grams.

Phenol is a colourless, crystalline substance which readily dissolves in alcohol, ether and benzene. Its molecular weight is 94.11; b.p., 182.2 °C; m.p., 40.9 °C; d_4^{45} , 1.0545; and n_D^{45} , 1.5402. Phenol forms the crystal hydrate $C_6H_5OH \cdot 0.5H_2O$, which melts at about 17 °C.

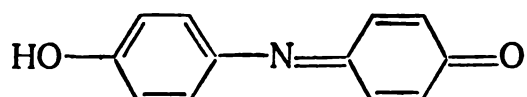
Phenol is poisonous to the nervous system, and it affects the skin. If some of it falls on the skin, the affected place should be washed with lime water.

Characterization Test. 1. When a few drops of a dilute ferric chloride solution are added to the aqueous phenol solution, a violet colour appears as a result of the formation of a strongly dissociated ferric phenoxide complex:



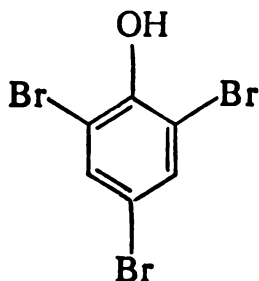
The colour disappears when the coloured solution is acidified.

2. A few drops of a dilute solution of ammonia and chlorinated lime are added to a dilute aqueous phenol solution. When the mixture is heated for a minute, a dark-blue colour appears and gradually becomes more and more intense as a result of the formation of a dye called indophenol:



The dark-blue colour turns bright red when hydrochloric acid is added to the mixture.

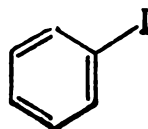
3. When a solution of phenol in water is acidified with dilute hydrochloric acid, and then bromine water is gradually added dropwise, a white precipitate called tribromophenol is formed:



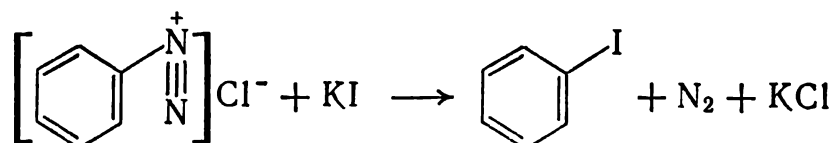
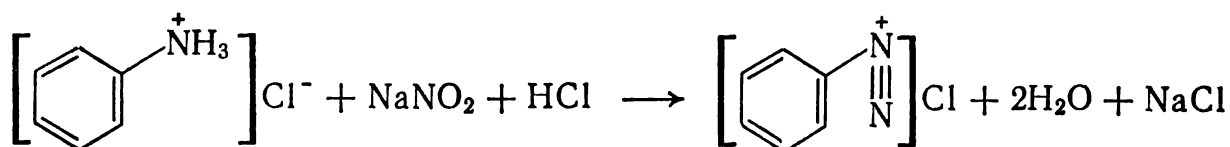
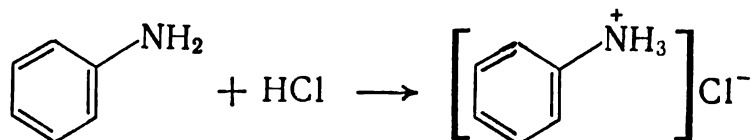
Toluidines, xylidines, aminophenols, and *m*-chloro- and *m*-nitro-anilines can be diazotized similarly.

IODOBENZENE

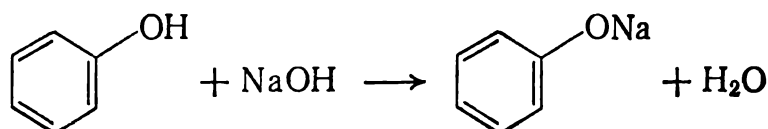
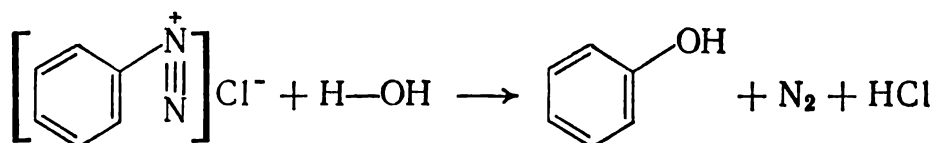
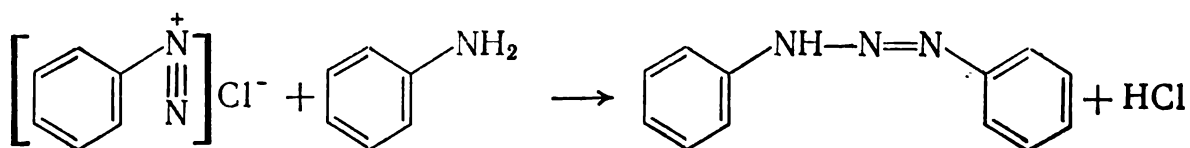
Formula:



Main reactions:



Side reactions:



Reagents and Equipment

Aniline	9.3 g or 9.2 ml (0.1 mole)	Beaker, thick-walled (300 ml)	1
Hydrochloric acid ($d = 1.19$)	25 ml (0.35 mole)	Funnel, dropping	1
Sodium nitrite	8 g (0.12 mole)	Flask, round-bottom (500 ml)	1
Potassium iodide	20 g (0.12 mole)	Condenser, air	1
Sodium hydroxide		Apparatus, steam distillation	1
Calcium chloride, anhydrous		Funnel, separatory	1
Ice		Flask, conical	1
		Flask, Würtz (50 ml)	1
		Thermometer	1
		Receivers	2

Assembly

1. A thermometer and a dropping funnel are put in a 300-ml thick-walled beaker which is placed in an icy bath. The end of the funnel should be immersed in the liquid by 1-2 cm.

2. A 500-ml round-bottom flask is connected to a reflux air condenser and placed in a water bath.

3. Steam distillation apparatus (see Fig. 3.6).
4. A 50-ml Würtz flask is connected to a thermometer and an air condenser, under whose other end is a receiver.

Procedure

Twenty-five millilitres of concentrated hydrochloric acid and the same amount of water are mixed in the thick-walled beaker of apparatus 1. Then 9.3 g of freshly distilled aniline are added to the solution. A cooled solution of 8 g of sodium nitrite in 20 ml of water is gradually added from a dropping funnel to the mixture, which is cooled with ice to 1-2 °C, while continuously stirring the mixture (for details, see p. 266).

The reaction mixture is diazotized while continuously cooling it. A few pieces of ice can be added to it if the temperature rises. Iodized starch paper is used to see whether the reaction has been completed. The end of diazotization should be strictly controlled because an excess of nitrous acid can reduce the iodobenzene yield.

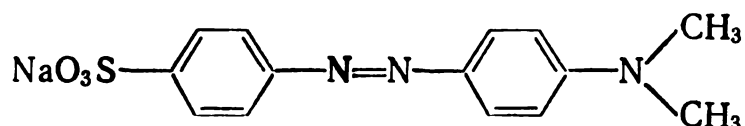
The diazonium salt solution obtained is mixed in the 500-ml round-bottom flask with a solution of 20 g of potassium iodide in 15 ml of water (excess potassium iodide hinders the formation of a by-product, i.e., phenol), and the mixture is allowed to cool for several hours. Afterwards, the flask is heated in a slightly boiling water bath (apparatus 2) until nitrogen is no longer liberated.

The solution is then alkalized with a concentrated sodium hydroxide solution until a highly alkaline reaction occurs so as to bind phenol (a by-product formed in the reaction) as sodium phenoxide. Iodobenzene is steam distilled until oily drops no longer drip from the condenser. Sodium phenoxide, unlike phenol, is not distilled with steam. The distillate is transferred to a separatory funnel and the lower layer of iodobenzene is separated from water and placed in a conical flask. The crude iodobenzene should be light yellow. If it is brown (due to the presence of free iodine), it is shaken with a small amount of a sodium sulphite or bisulphite solution in a separatory funnel until the mixture becomes clear. Then the lower layer is separated again. Iodobenzene is dried over anhydrous calcium chloride and distilled by heating the flask (apparatus 4) on an asbestos gauze. The fraction which boils at 185-190 °C is collected. Iodobenzene can be distilled under vacuum. Its yield is about 16 g.

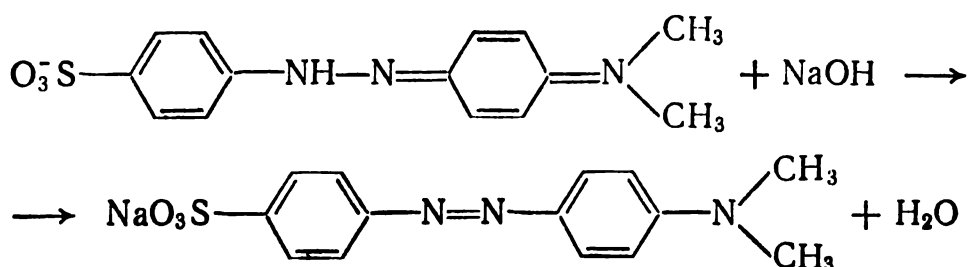
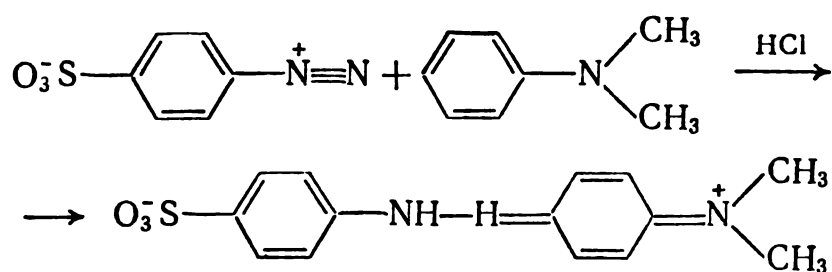
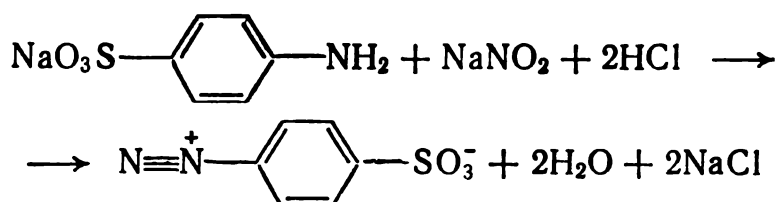
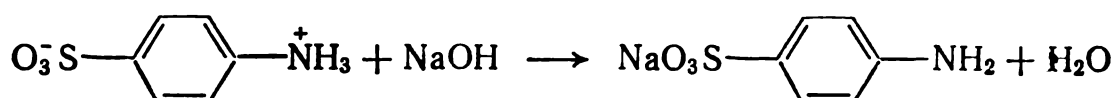
Iodobenzene is a liquid with a peculiar odour, insoluble in water, but well soluble in alcohol. Its molecular weight is 204.01; b.p., 188.45 °C; m.p., -31.35 °C; d_4^{15} , 1.8382; and n_D^{18} , 1.6213. It is used for synthesizing ethylbenzene and benzoic acid,

HELIANTHIN

Formula:



Main reactions:

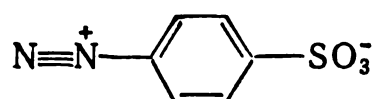
**Reagents and Equipment**

Sulphanilic acid	5 g (0.025 mole)	Beakers (125 and 500 ml)	2
Sodium nitrite	2 g (0.03 mole)	Flask, Bunsen	1
Sodium hydroxide, 2 <i>N</i> solution	12.5 ml	Funnel, Büchner	1
Hydrochloric acid, 2 <i>N</i> solution	12.5 ml	Flask, safety	1
Hydrochloric acid, 1 <i>N</i> solution	25 ml		
Dimethylaniline	3 g or 3 ml (0.025 mole)		

Procedure

Five grams of crystalline sulphanilic acid are dissolved in 12.5 ml of a 2 *N* sodium hydroxide solution in a 125-ml beaker while slightly heating. Since sulphanilic acid dissolves sparingly in water, it is converted into the soluble sodium salt

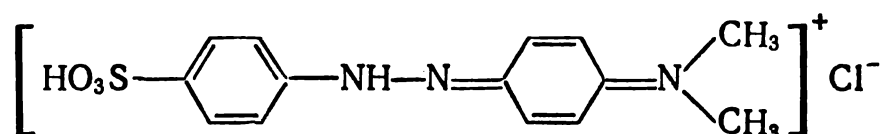
$\text{NaO}_3\text{S}-\text{C}_6\text{H}_4-\text{NH}_2$. When all the acid dissolves, the liquid should produce an alkaline reaction (by the litmus test). The solution obtained is cooled with water, 2 g of sodium nitrite in 25 ml of water are added, and the mixture is stirred until sodium nitrite completely dissolves. Afterwards, the solution is cooled with ice and poured, while stirring, into the 500-ml beaker containing 12.5 ml of a 2 *N* hydrochloric acid solution. A few minutes later, the white powdery diazonium salt precipitates as a bipolar ion:



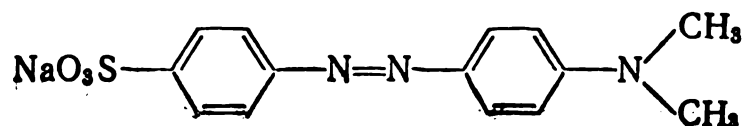
The product obtained is not separated, but is used as a suspension. It is more stable than the other diazonium salts, and can be stored for several hours.

Three millilitres of freshly distilled dimethylaniline are dissolved in 25 ml of a 1 *N* hydrochloric acid solution in a small beaker. All the dimethylaniline should dissolve. This will be evident from the absence of an oily layer on the solution. The solution obtained is added to a suspension of the diazotized sulphanilic acid, which is in a 500-ml beaker, and the mixture is stirred well. In 5-10 min, a thick paste of a red acid-resistant dye modification is formed. To convert it into sodium salt, a 2 *N* sodium hydroxide solution is added to the paste until a highly alkaline reaction occurs. The mixture is stirred well and heated until it boils. In this case, the larger part of the dye passes into solution.

In an alkaline medium, helianthin is yellow, in a neutral medium, it is orange, and in an acid medium, red. It changes colour at pH 3.2-4.4 as a result of the conversion of one chromophore (C_6H_4 of the quinoid structure) into another ($-\text{N}=\text{N}-$ azo group). Thus, red helianthin has a quinoid structure:



When alkali is added to it, yellow helianthin is formed with the azo group



The mixture is cooled in icy water and the orange crystals of the sodium salt of the dye which have precipitated are filtered off in the Büchner funnel.*

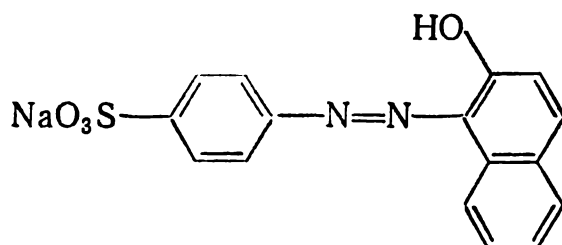
The product can immediately be recrystallized from a small amount of water.

Helianthin (methyl orange, sodium 4-dimethylaminoazobenzene-4'-sulphonate, orange III) consists of crystals which are in the form of scales or powder. Its molecular weight is 327.34. It is a commonly used acid-alkali colour indicator.

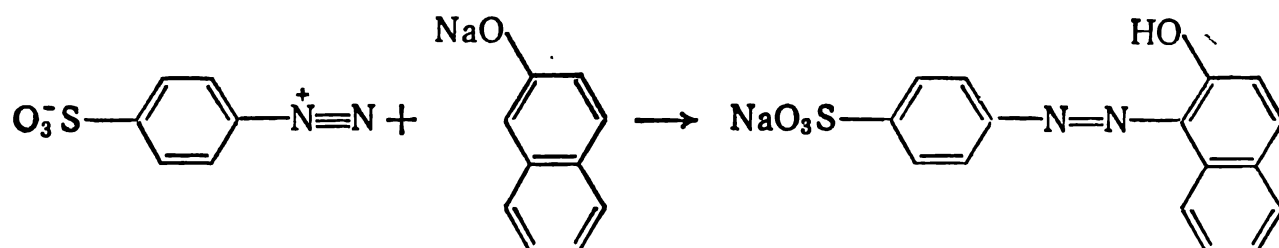
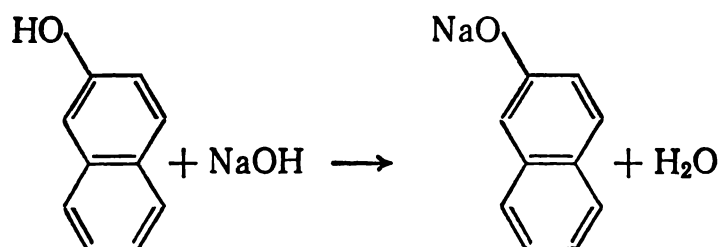
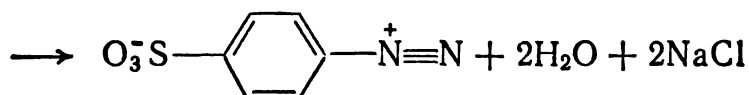
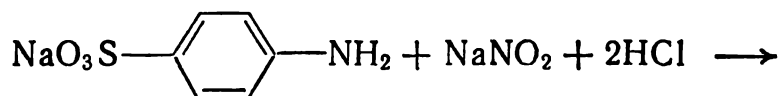
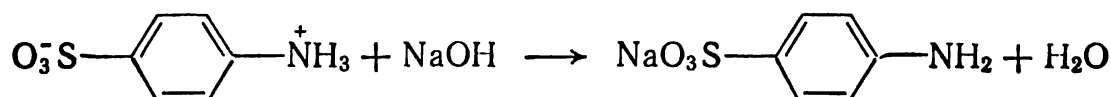
Characterization Test. When hydrochloric acid is added to a not very dilute solution of the dye, the solution turns pink and red-brown crystals precipitate.

β-NAPHTHOL ORANGE

Formula:



Main reactions:



* It is better to use a saturated sodium chloride solution for rinsing the beaker. The hands should be washed with a warm potassium permanganate solution, which is slightly acidified with sulphuric acid, until they are coloured with manganese dioxide. The colour should then be removed with a warm, dilute sodium bisulphite solution,

Reagents and Equipment

Sulphanilic acid	5 g (0.025 mole)	Beakers	2
Sodium nitrite	2 g (0.03 mole)	Flask, Bunsen	1
β -Naphthol	3.6 g (0.025 mole)	Funnel, Büchner	1
Sodium hydroxide, 2 <i>N</i> solution	12.5 ml	Flask, safety	1
Hydrochloric acid, 2 <i>N</i> solution	12.5 ml		
Sodium hydroxide	2 g		
Sodium chloride	25 g		

Procedure

Sulphanilic acid is diazotized in the same way as when helianthin is being obtained (see p. 271). In a beaker, 2 g of sodium hydroxide are dissolved in 40 ml of water, and then 3.6 g of β -naphthol are added to the solution obtained. The suspension of diazotized sulphanilic acid is poured in while stirring the solution. Continue stirring for 30 min. Then, in order to reduce dye solubility, 25 g of sodium chloride are added and the beaker is allowed to stand in ice for one hour while stirring the mixture from time to time. The dye which has precipitated is sucked off (see Fig. 2.21), washed with a small amount of cold water, strongly wrung in the Büchner funnel, removed from the filter and dried in air. The β -naphthol orange yield is about eight grams.

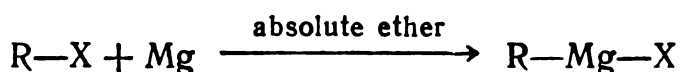
β -Naphthol orange (acid orange, orange II) is a bright orange, crystalline substance which dissolves well in water. Its molecular weight is 350.34. This dye is used owing to its bright shade and good fastness.

Chapter 16

GRIGNARD REACTIONS

Grignard reactions are the syntheses of several organic compounds with mixed organomagnesium halides.

Magnesium was first used in organic synthesis in 1899, by P. A. Barbier, for synthesizing tertiary alcohols, which had been obtained first with the aid of organic zinc compounds by A. M. Butlerov. In 1900 V. Grignard, Barbier's pupil, perfected this reaction. He discovered that in a dry ethereal medium magnesium reacts with many alkyl and aryl halides to form mixed organomagnesium halides (Grignard's reagents). These are usually called organomagnesium compounds:

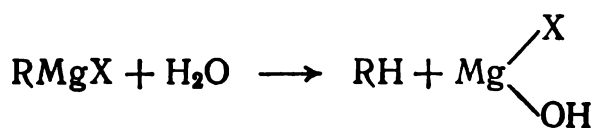


where R = alkyl, aryl, etc.;
X = halogen.

These compounds are very active chemically and capable of entering into diverse reactions.

The most important conditions for carrying out Grignard reactions are the cleanliness of the apparatus and the thorough purification of reagents. It is especially necessary to remove substances which contain a mobile (active) hydrogen atom (particularly water, acids and alcohols) by washing the halide several times with water, drying it over calcium chloride and distilling it immediately before it is used in a reaction.

Water decomposes organomagnesium compounds, resulting in the formation of the appropriate hydrocarbons:

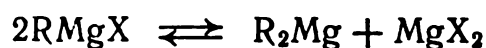


Alcohols and carboxylic acids act similarly.

Absolute ethyl ether is the solvent most commonly used for the Grignard reaction. It should be stored in dark bottles over sodium whose surface should be lustrous. Dipropyl, diisopropyl, dibutyl, diamyl and diisoamyl ethers may also be used when the reaction mixture must be heated to a temperature higher than the boiling point of ethyl ether. By attaching themselves to organomagnesium compounds, ethers besides being solvents, also form complexes.

These complexes, called etherates, can be separated as crystals. They dissolve well in ethyl ether, thus disengaging the surface of the magnesium which continues to react.

Organomagnesium compounds in an ethereal solution are in a state of mobile equilibrium and regarded as a mixture of mixed RMgX and simple R_2Mg organomagnesium compounds:



Equilibrium shifts to either one side or the other, depending on the reaction conditions. Equilibrium depends on the quantity of the radical: the greater the molecular weight of the alkyl of an organomagnesium compound, the more does equilibrium shift towards the formation of dialkylmagnesium, R_2Mg .

In the Grignard reaction, the rate at which alkyl halides interact decreases from iodides to chlorides, although chlorides and bromides give better yields than iodides. This is due to a side reaction, which occurs at the highest rate when iodides are involved:



An exception is methyl iodide, CH_3I , which is widely used for the Grignard reaction.

When work is being done with readily reacting alkyl bromides and iodides, chips of magnesium are used; with substances which react with greater difficulty, use magnesium in the form of minute filings or even powder.

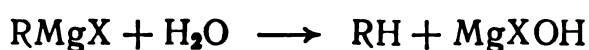
In many cases, magnesium must be activated, especially when aryl halides are introduced into a reaction. Iodine is commonly used as an activating agent. A small amount of an ethereal solution of a halide is added to a calculated amount of magnesium in absolute ether. If the reaction does not begin even when the flask is heated, a small iodine crystal is put in. The solution then becomes turbid, and the ether boils as a result of the heat evolved in the reaction. Afterwards, the ethereal solution of a halide is added dropwise at such a rate that the ether continues to boil uniformly.

Magnesium can be activated during the reaction also by another method, i.e., by means of reactive alkyl halides, such as ethyl bromide. This must be done when slightly active halides, together with magnesium, form organomagnesium compounds which are sparingly soluble in ether, and which cover the magnesium surface and hinder the further interaction between magnesium and the original halide. When ethyl bromide is added, it reacts with magnesium, forming ethylmagnesium bromide ($\text{C}_2\text{H}_5\text{MgBr}$). The magnesium surface is then cleansed from the sparingly soluble organomagnesium compound. To carry out this reaction, excess magnesium is used with respect to the original halide.

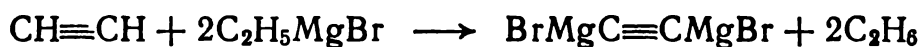
Since organomagnesium compounds can react with various organic and inorganic compounds, they are very important for making preparations in organic chemistry, especially for obtaining alcohols, acids, aldehydes, ketones and hydrocarbons.

16.1. PREPARATION OF HYDROCARBONS

Organomagnesium compounds readily react with substances which contain an active hydrogen atom, such as water, alcohols, phenols, oximes, amines (including heterocyclic compounds, i.e., pyrrole and indole), acids, amides, mercaptans, acetylene and monoalkylacetylenes, forming hydrocarbons, e.g.,



This reaction can be used also for obtaining organomagnesium compounds which ordinarily (i.e., when magnesium acts on the appropriate halides) are obtained either with difficulty or not at all. For instance, a magnesium bromide or a magnesium iodide derivative of acetylene is obtained when acetylene interacts with ethylmagnesium bromide or iodide:



In 1902, L. A. Chugaev proposed using methylmagnesium iodide for quantitatively determining the hydroxyl and other groups which contain an active hydrogen atom:



F. V. Tserevitinov used these reactions to work out a method (apparatus) for quantitatively determining active hydrogen in organic compounds by the volume of the methane produced. Later, it was modified somewhat by A. P. Terentiev.

This method of determining the active (mobile) hydrogen atom is now called the Chugaev-Tserevitinov method.

Thus, reactions between organomagnesium compounds and compounds containing an active hydrogen atom are very important. They are used for qualitatively and quantitatively determining the functional groups which contain an active hydrogen atom, for obtaining hydrocarbons from the halides and from the organomagnesium compounds belonging to the series of acetylene, fluorene, pyrrole, indole, etc.

QUANTITATIVE DETERMINATION OF ACTIVE HYDROGEN BY THE CHUGAEV-TSEREVITINOV METHOD

This method is based on the interaction between the test substance and methylmagnesium iodide:



In this case, an equimolecular amount of methane is evolved. Its volume is measured by a burette. The reaction is usually carried out in amyl ether, anisole, xylene and pyridine. Ethyl ether can be used if the reaction occurs readily at 20 °C.

All the reagents used in analysis should be thoroughly dehydrated since methylmagnesium iodide decomposes in the presence of moisture.

Reagents and Equipment

Anisole	19.9 g or 20 ml (0.18 mole)	Flask, round-bottom (100 ml)	1
Magnesium chips . .	2 g (0.08 gram atom)	Condenser, Liebig	1
Methyl iodide . . .	6.9 or 3 ml (0.04 mole)	Tube, calcium chloride . . .	1
		Receiver	1
Iodine			

Preparation of Grignard's Reagent (Methylmagnesium Iodide).

Put 20 ml of anisole, two grams of magnesium chips which have been dried in a drier for ten minutes, three millilitres of methyl iodide and several small iodine crystals in the 100-ml round-bottom flask. The mixture is slightly heated if a reaction does not begin at room temperature. After the reaction, attach a reflux condenser fitted with a calcium chloride tube to the flask and heat the mixture for one hour in a boiling water bath. Then, unreacted methyl iodide is driven off after replacement of the reflux condenser with a downflow one. The methylmagnesium iodide solution is decanted from the magnesium which remains after the reaction and stored in a bottle that is closed well with a cork stopper covered with paraffin. The solution may be stored for three or four weeks.

Procedure

The apparatus for determining active hydrogen (Fig. 16.1) consists of a reaction vessel 1 with a methylmagnesium iodide reservoir 2. Vessel 1 is connected by rubber tubing to a gas burette 4, in which the methane being liberated is collected and its volume measured. The reaction vessel 1 and the gas burette 4 are placed in water baths 3 and 6 with the same temperature.

Before starting the analysis, dry air or dry nitrogen is passed through the reaction vessel for 15 min, since the apparatus must be absolutely dry if exact results are to be obtained.

After securing the reaction vessel 1 vertically in a stand 100-200 mg of the test substance are put into it through funnel 9. Then, 3.5 ml of anisole are poured through the funnel into the vessel, trying to wash the residues of the substance off the funnel into the vessel. When the substance dissolves, 5 ml of a prepared Grignard's reagent are carefully put into the reservoir 2 by means of a bent funnel 10. The reaction vessel is then closed well with a

rubber stopper having an outlet tube 5 which is connected to the gas burette 4.

Next, in order to maintain constant temperature, the reaction vessel is put in a water bath 3. When the temperatures of the water bath 3 and the water bath 6 (in which the burette 4 is placed) equalize (in about 10 min), the stopcock 7 is taken out quickly and then immediately put back. This must be done in order to create atmospheric pressure in the reaction vessel. The stopcock 7 is then so turned that the burette is open to the atmosphere. The levelling bulb filled with mercury 8, which forces all the air out of the burette, is raised.

The stopcock 7 is turned at a right angle, and the levelling bulb is lowered and secured in a stand. The water bath is removed and the reaction vessel is so tilted that all the methylmagnesium iodide flows out of the reservoir 2 and into the vessel 1, which contains the test substance. Methane is then liberated; under its pressure, the level of mercury in the burette drops. As soon as this level begins to drop more slowly, the vessel 1 is heated to 90°C in a water bath to complete the reaction. When the vessel has cooled, it is put in a water bath at room temperature. The levels in the burette and in the bulb 8 are equalized in ten minutes. The volume of the gas collected, and the temperature and barometric pressure are then measured. The gas volume is reduced to standard conditions.

The content of active hydrogen x (in percentage with respect to weight) is calculated by the following formula:

$$x = \frac{0.000719 \times Y \times 1.008}{16a} \times 100$$

where 0.000719 = mass of 1 ml of methane at 0°C and 760 mm Hg;
 Y = volume of methane reduced to 0°C and 760 mm Hg;

1.008 = atomic weight of hydrogen;

16 = molecular weight of methane;

a = weighed sample of the test substance, g.

The permissible error is up to 10 per cent.

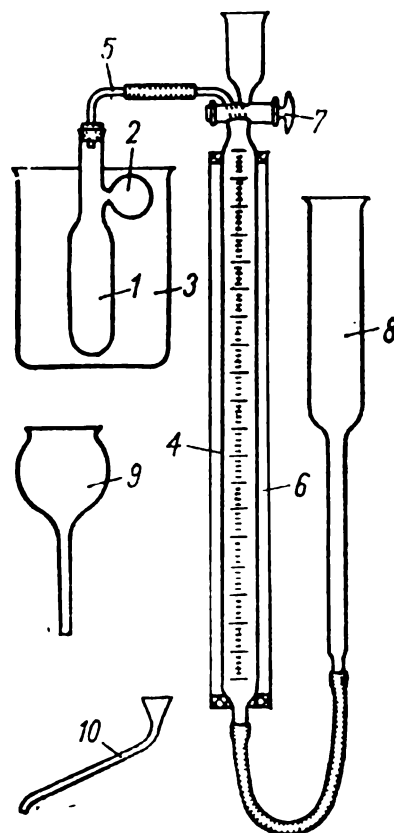
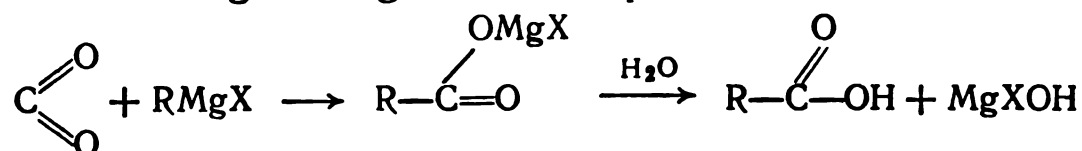


Fig. 16.1. Apparatus for quantitatively determining active hydrogen by the Chugaev-Tserevitinov method:

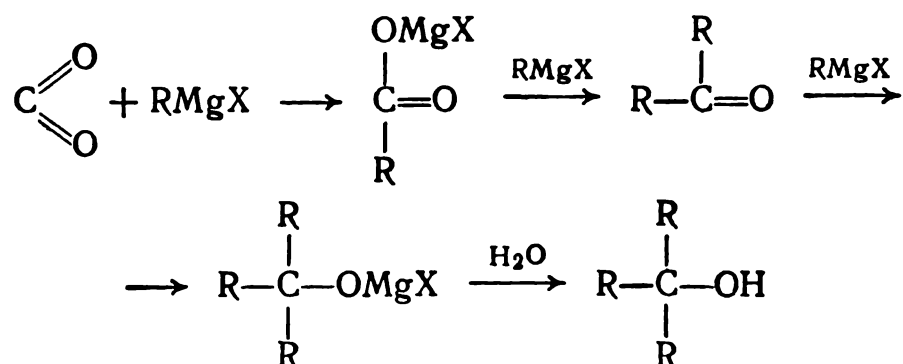
1—reaction vessel; 2—reservoir for methyl-magnesium iodide; 3—water bath; 4—gas burette; 5—outlet tube; 6—water jacket of the gas burette; 7—stopcock; 8—levelling bulb; 9, 10—funnels

16.2. PREPARATION OF CARBOXYLIC ACIDS

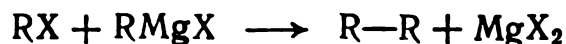
Carboxylic acids are formed when Grignard's reagent is poured on dry ice or when carbon dioxide is passed through the ethereal solution of an organomagnesium compound:



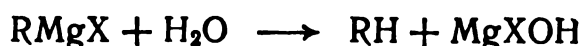
The carbon dioxide must be dried thoroughly and supplied very slowly to the reaction medium. Otherwise, a side reaction occurs, resulting in the formation of ketones and tertiary alcohols:



Moreover, the hydrocarbon $\text{R}-\text{R}$ is formed at the initial stage of the reaction:



When the reaction mixture is decomposed with water, the hydrocarbon RH is formed:



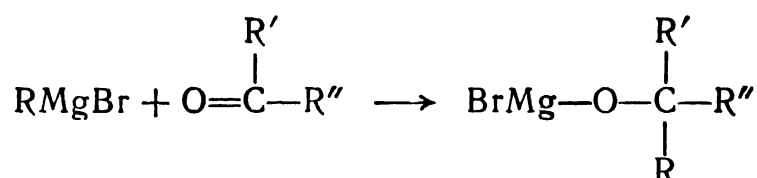
The yield can be increased by carrying on the reaction while it is being greatly cooled. To this end, pieces of solid carbon dioxide are added to the ethereal solution of an organomagnesium compound. To separate the carboxylic acid formed from the by-products (ketone, tertiary alcohol and hydrocarbons), the entire reaction product is treated with aqueous alkali until an alkaline reaction occurs. The acid passes as salt into the aqueous solution and is separated from insoluble impurities in a separatory funnel. A mineral acid is added until a clearly acid reaction occurs, and the organic acid is extracted with ether and then processed as usual.

16.3. PREPARATION OF ALCOHOLS

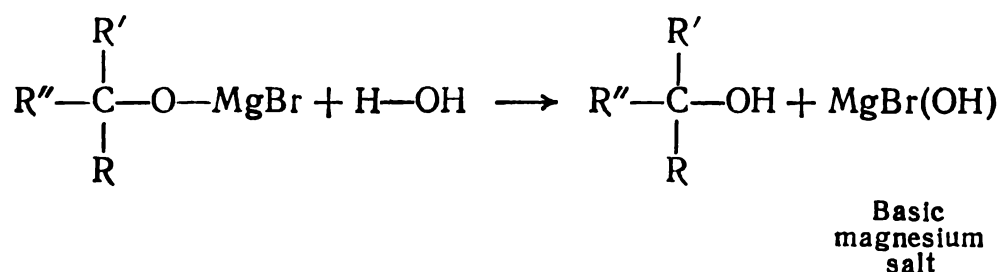
Alcohols are formed when organomagnesium compounds interact with aldehydes, ketones and esters that have the carbonyl

group $\text{—}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}=\text{O}$ with an electron cloud $\text{—}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}=\text{O}$ which is shifted

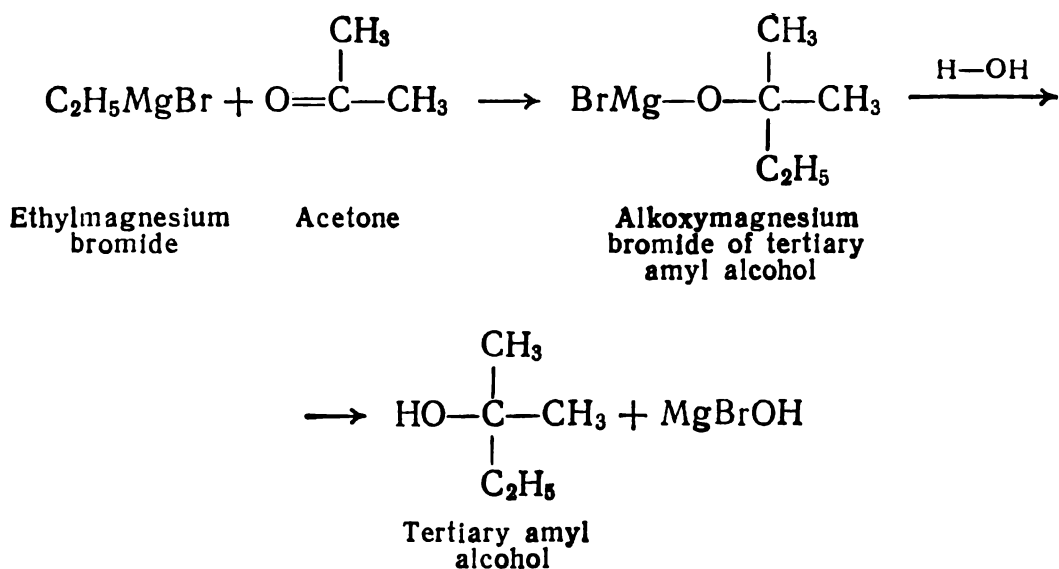
towards the oxygen atom. Consequently, a certain positive charge originates at the carbon atom, and a partially negative one at the oxygen atom. In magnesium alkyl halide, RMgBr , the radical R acts as a nucleophilic particle which is readily bonded to the carbon of the carbonyl group:



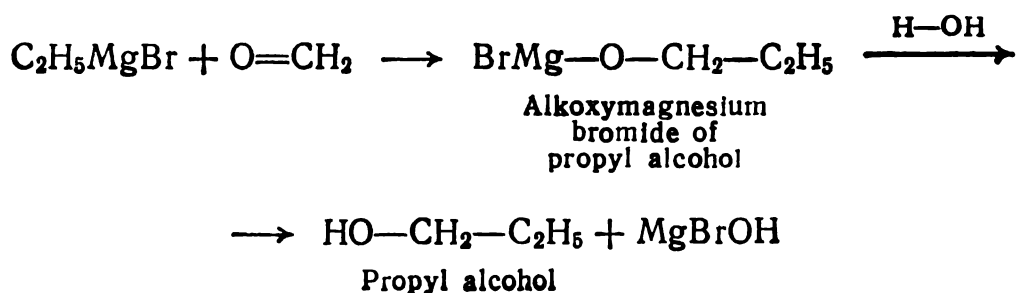
The alkoxymagnesium bromide obtained is hydrolyzed with water, and alcohol is obtained:



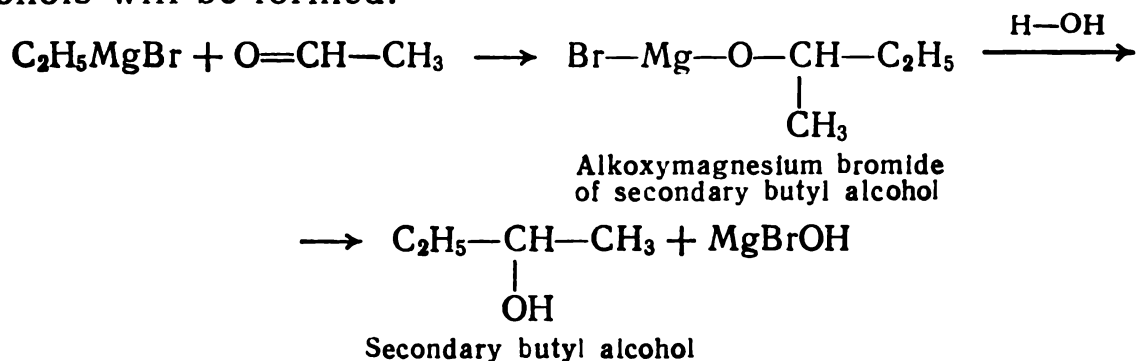
When ketones react with organomagnesium compounds, tertiary alcohols are formed:



If formaldehyde is the initial carbonyl compound in a reaction, the reaction products will be primary alcohols:



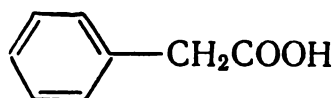
If other aldehydes are introduced into the reaction, secondary alcohols will be formed:



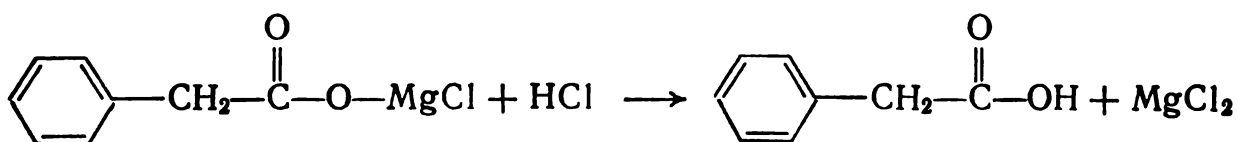
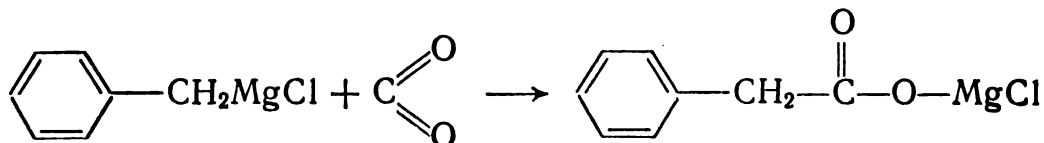
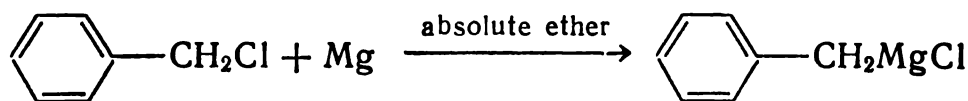
16.4. SYNTHESSES

PHENYLACETIC ACID

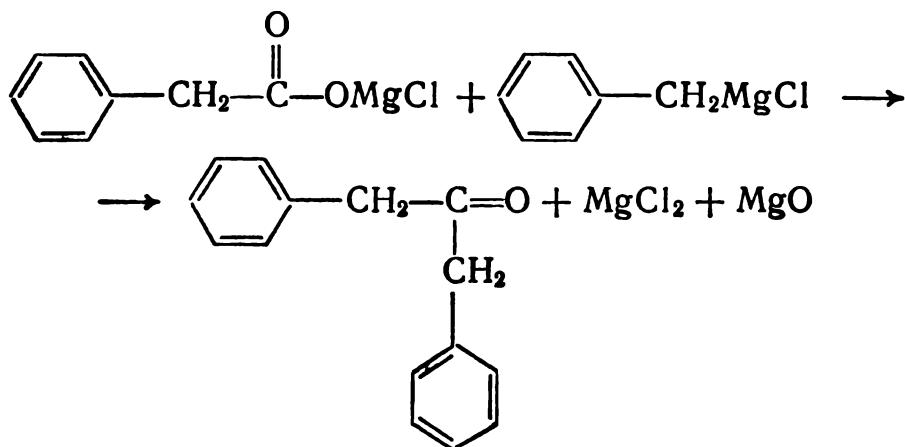
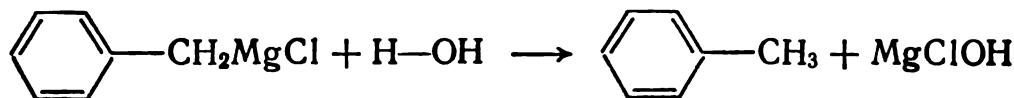
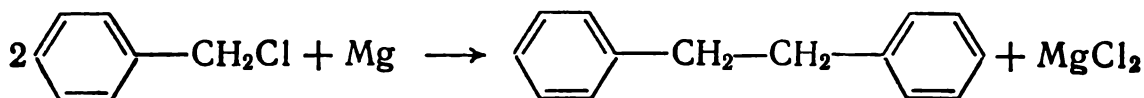
Formula:



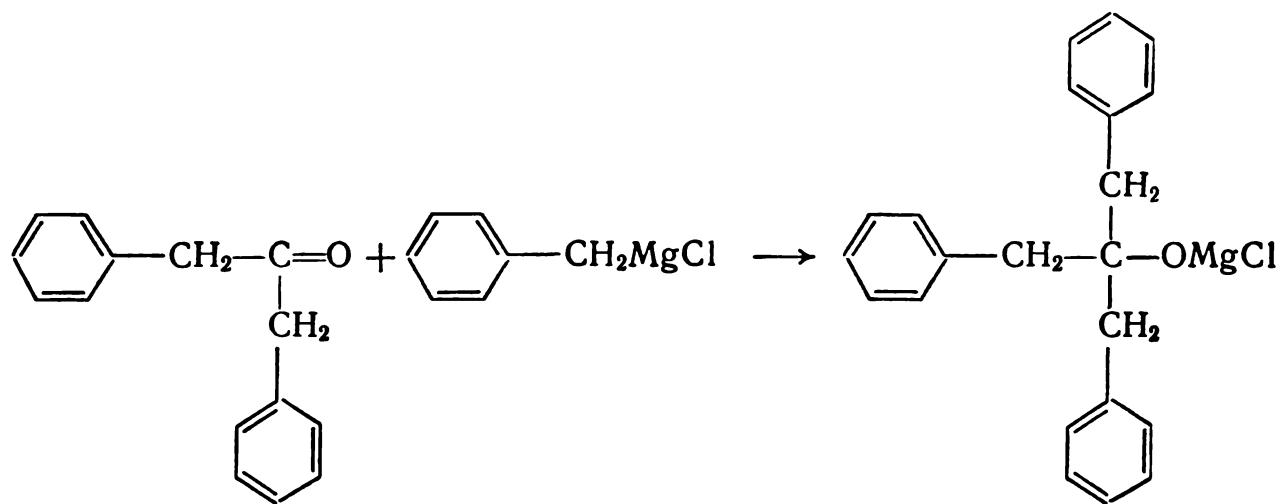
Main reactions:



Side reactions*:



* The reactions given below may occur, but not necessarily.



Reagents and Equipment

Benzyl chloride	12.7 g or 11.5 ml (0.1 mole)	Flask, round-bottom (250 ml)	1
Magnesium, metallic (chips, filings)	2.4 g (0.1 gram atom)	Funnel, dropping	1
Absolute ethyl ether	70 ml	Funnel, separatory	1
Hydrochloric acid ($d = 1.19$)	10 g or 8.4 ml	Head, still	1
Ethyl ether	40 ml	Condenser, Liebig	1
Iodine, crystalline	0.1-0.2 g	Bottles, Tishchenko	2
Carbon dioxide		Tubes, calcium chloride	2
		Flask, Bunsen	1
		Funnel, Büchner	1
		Flask, safety	1
		Generator, Kipp	1

Assembly

1. A 250-ml round-bottom flask is placed in a water bath and closed well with a cork stopper which has a still head (rubber stoppers swell under the action of ether). A dropping funnel is secured in the straight neck of the adapter, and a reflux condenser, in the side neck. Both the condenser and the dropping funnel must be closed with calcium chloride tubes. The entire apparatus must be absolutely dry. The stoppers should not be lubricated with glycerol.

2. The dropping funnel is replaced with a gas inlet tube adjusted beforehand. One end of the tube reaches almost the bottom of the flask, while the other end is connected through the Tishchenko bottles to the Kipp generator (or a gas cylinder).

3. Suction apparatus (see Fig. 2.21).

Procedure

A few small iodine crystals and 2.4 g of magnesium filings are put in the 250-ml round-bottom flask, and a solution of 12.7 g of pure benzyl chloride in 70 ml of absolute ether is added dropwise through the dropping funnel.

1. Magnesium must be activated with iodine when alkyl halides which react with difficulty are introduced into the reaction. *Care should be taken to avoid getting iodine on the skin.*

2. Magnesium must be dried at first for 30 min at 60-80 °C, and then in a vacuum desiccator. It must be stored in airtight glass bottles.

3. *Benzyl chloride* irritates the mucous membranes and, in large concentrations, is *toxic*.

When one-third of the benzyl chloride solution has been added, a spontaneous exothermic reaction begins. During the reaction, the ether boils, the solution becomes turbid and iodine colour disappears. If the spontaneous reaction is delayed, it means that the reagent is not quite pure. In this case, the bath must be heated slightly. When the reaction begins, heating must be stopped.

The ethereal solution of benzyl chloride should then be added at such a rate that the ether boils slightly. In this case, the ethereal condensate should run out of the reflux condenser not in a continuous stream, but in consecutive drops. Care should be taken not to introduce large portions of the solution since the reaction may become too vigorous. As a result, a large amount of by-products may be formed and, consequently, the phenylacetic acid yield may decrease.

When all the ethereal solution of benzyl chloride has been put in, boiling gradually ceases. The contents of the flask are then heated in a water bath for another 0.5 h. In this case, only an insignificant amount of magnesium, i.e., that taken in excess, may remain unchanged. When a large amount of unreacted magnesium remains in the residue, it means that the reaction was too vigorous or the reagents were not sufficiently pure and dry. In such cases, the beginning of the spontaneous reaction is retarded.

The flask is then intensively cooled from the outside with a mixture of ice and salt (or water and crushed ice). Carbon dioxide from the Kipp generator or from a cylinder is passed for two or three hours through the ethereal solution of an organomagnesium compound (the solution is usually turbid, grey or brown). The gas is thoroughly dried by passing it through two Tishchenko bottles containing concentrated sulphuric acid. Carbon dioxide must be supplied very slowly, or a side reaction may occur.

1. Saturation with carbon dioxide should be carried out at a temperature ranging from -10 °C to 0 °C because the gas interacts exothermically with an organomagnesium compound and may cause a large amount of ether to evaporate.

2. The phenylacetic acid yield can be increased by introducing solid carbon dioxide into the reaction. In this case, Grignard's reagent is decanted on dry ice.

3. Ether begins to boil due to the heat evolved in the reaction. The reaction ends when the ether ceases to boil.

The flask containing the solution is cooled again by putting 15-20 g of ice into it. When the reaction has ended, the gas inlet

tube is replaced with a dropping funnel. The reaction product coming out of the dropping funnel is hydrolyzed with acidified water, i.e., 10 g of HCl ($d = 1.19$) in 20 ml of water, until congo red shows an acid reaction. Then, some more ether is added if much of it has evaporated during the reaction. The reaction mixture separates into two clear layers, which are then separated from one another in a separatory funnel. The aqueous solution is extracted twice with ether (20 ml every time). The combined ethereal solutions of phenylacetic acid are treated with a dilute sodium hydroxide solution until the solution reacts alkaline, thus freeing the acid from the by-products.

When a sodium hydroxide solution is added, phenylacetic acid turns into a water-soluble salt. The neutral products, which are impurities, remain in the ethereal solution.

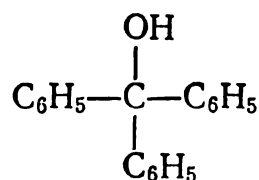
The lower alkaline solution is separated from the ether and then acidified with a 10 per cent HCl solution and cooled. Before acidifying the solution, boil it down in order to free it from the dissolved ether. The phenylacetic acid which has precipitated is sucked off in the Büchner funnel. If the product is not quite pure, it is recrystallized from hot water. The phenylacetic acid yield is about eight grams.

Phenylacetic acid is a light yellow or light green crystalline powder. Its molecular weight is 136.15; b.p., 265.5 °C, and m.p., 72-77 °C. The acid dissolves sparingly in cold water and better in hot water. It dissolves well in alcohol and ether. It is used in organic synthesis.

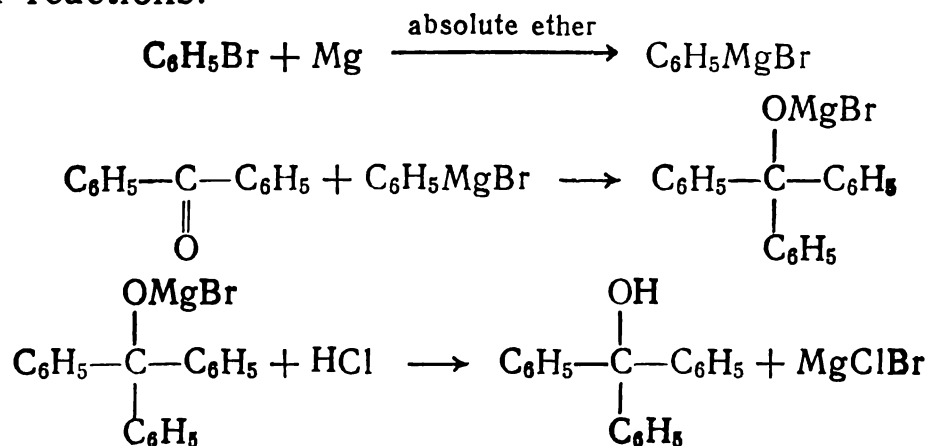
Characterization Test. When phenylacetic acid is heated together with concentrated sulphuric acid, it decomposes with the liberation of carbon dioxide.

TRIPHENYLCARBINOL

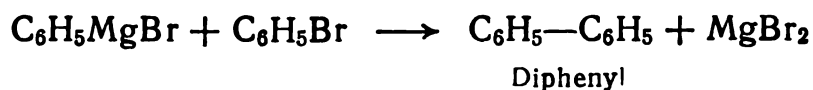
Formula:



Main reactions:



Side reaction:



Reagents and Equipment

Bromobenzene	20 g or 13 ml (0.12 mole)	Flask, round-bottom with 3 necks (300 ml)	1
Magnesium, metallic (chips)	3 g (0.12 gram atom)	Stirrer	1
Absolute ethyl ether . . .	80 ml	Condenser, Liebig	1
Benzophenone	18.2 g (0.1 mole)	Funnel, dropping	1
Ethyl ether	40 ml	Funnel, separatory	1
Iodine		Tube, calcium chloride . . .	1
Hydrochloric acid		Flask, Würtz (300 ml) . . .	1
Sodium bicarbonate		Thermometer	1
		Adapter, bent	1
		Receiver	1
		Apparatus, steam distillation	1
		Flask, Bunsen	1
		Funnel, Büchner	1
		Flask, safety	1

Assembly

1. A 300-ml round-bottom flask with 3 necks, placed in a water bath, is fitted with a stirrer, a dropping funnel and a reflux water condenser having a calcium chloride tube.

2. A 300-ml Würtz flask is placed in a water bath and fitted with a thermometer and a Liebig condenser having a bent adapter, whose end is put into a receiver.

3. Steam distillation apparatus (see Fig. 3.6).

4. Suction apparatus (see Fig. 2.21).

Procedure

Three grams of magnesium filings and a few small iodine crystals are put into the 300-ml round-bottom flask with 3 necks. Afterwards, 15 ml of absolute ether and one-third of a solution (13 ml) of bromobenzene in 40 ml of absolute ether are added. In a few minutes, a spontaneous reaction begins and the ether boils (see p. 284). When the reaction is delayed, it means that the reagents are not quite pure. When the spontaneous reaction begins, the remaining ethereal solution of bromobenzene is gradually poured through the dropping funnel into the flask while so regulating its supply that the ether boils intensely, but not too vigorously. When all the ethereal solution of bromobenzene has been added, the reaction mixture is heated in a water bath, allowing the ether to boil slightly for 30 min.

The reaction is considered complete when only a few small pieces of magnesium remain (see p. 284), and the solution turns turbid or brown.

The flask containing the phenylmagnesium bromide obtained is then cooled from the outside with cold water and ice, and a cooled solution of 18.2 g of benzophenone preliminarily dissolved in 25 ml of ether is slowly added. Next, the flask is heated for 30 min in a water bath. The flask is then cooled again with water and ice and the reaction product is hydrolyzed with cold water without dismantling the apparatus, continuously stirring the solution. Afterwards, a minimum amount of 50 per cent hydrochloric acid, necessary for completely dissolving the basic magnesium salt precipitate, is added.

The water and ethereal layers obtained are separated in a separatory funnel. An ethereal extract (20 ml) is then obtained from the water layer. The ethereal extract is washed with a sodium bicarbonate solution to remove the yellow colour. Then, the ether is driven off in a water bath (apparatus 2). Afterwards, the mixture is distilled with steam in order to remove unreacted bromobenzene and the diphenyl formed as a by-product.

The triphenylcarbinol which remains as a crystalline mass in the flask is sucked off in the Büchner funnel and dried. The triphenylcarbinol yield is about 13 g.

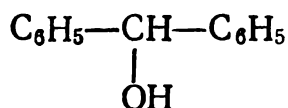
Triphenylcarbinol is a colourless crystalline product which melts at 162 °C and readily recrystallizes from alcohol, benzene or ligroin.

Characterization Test. When a small triphenylcarbinol crystal is put into a test tube containing 2 ml of concentrated sulphuric acid, a yellow colour appears:

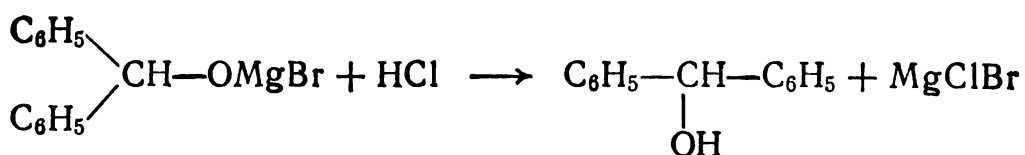
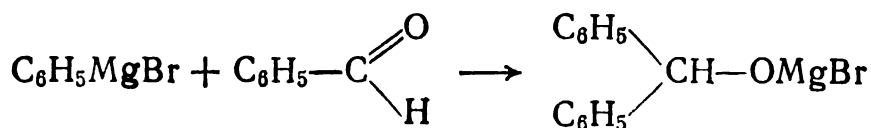
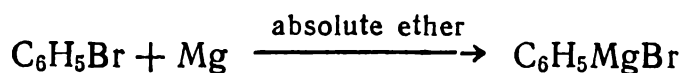


DIPHENYLCARBINOL (BENZHYDROL)

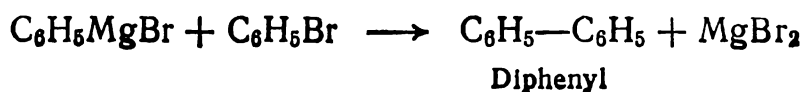
Formula:



Main reactions:



Side reaction:



Reagents and Equipment

Bromobenzene	23.5 g or 16 ml (0.14 mole)	Flask, round-bottom with 3 necks (500 ml)	1
Magnesium, metallic (chips)	3.6 g (0.14 mole)	Stirrer	1
Benzaldehyde	11.9 g or 11 ml (0.11 mole)	Funnel, dropping	1
		Funnel, separatory	1
Absolute ethyl ether	100 ml	Condenser, Liebig	1
Hydrochloric acid ($d = 1.19$)	12 ml	Tube, calcium chloride	1
Ethyl ether	40 ml	Flask, Würtz (300 ml)	1
Sodium bisulphite, 40 per cent solution	10 ml	Thermometer	1
Sodium bicarbonate		Adapter, bent	1
Iodine		Receiver	1

Assembly

1. A 500-ml round-bottom flask with 3 necks, placed in a water bath, is fitted with a stirrer, a dropping funnel and a reflux water condenser having a calcium chloride tube.

2. A 300-ml Würtz flask is placed in a water bath and fitted with a thermometer and a Liebig condenser having a bent adapter which is put into the receiver.

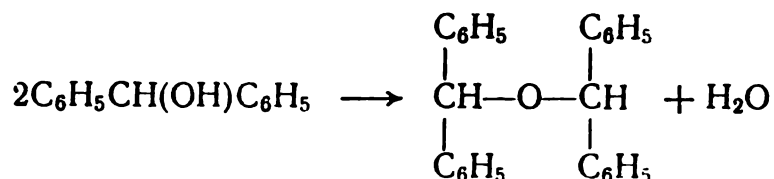
Procedure

Magnesium chips weighing 3.6 g are put into the 50-ml round-bottom flask with 3 necks of apparatus 1; then 20 ml of absolute ethyl ether are poured in and a small iodine crystal is added. Next, one-third of a solution of 16 ml of bromobenzene in 50 ml of absolute ether is introduced from a dropping funnel, waiting for a spontaneous reaction. If it does not occur, the solution is heated slightly (see p. 284). The remaining ethereal solution of bromobenzene is then added from the dropping funnel so that the ether boils moderately. When all the bromobenzene solution has been added, the flask is heated in a water bath for 0.5-1 h. At the end of the reaction, only an insignificant amount of magnesium residues is in the flask.

While stirring the cooled phenylmagnesium bromide solution obtained and cooling it from the outside, a solution of 11 ml of freshly distilled benzaldehyde in 30 ml of absolute ethyl ether is gradually added from a dropping funnel. Benzaldehyde must not be taken in excess. Otherwise, side reactions occur with the formation of ketone and primary and secondary alcohols.

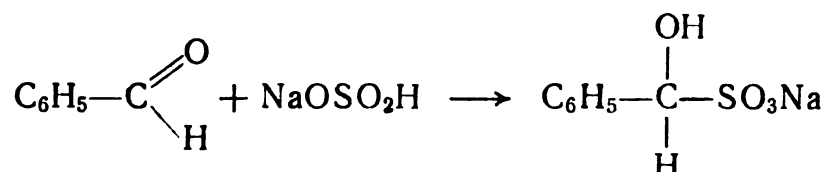
When all the benzaldehyde has been added, the flask is heated for 30 min in a water bath so as to bring the reaction to an end. The flask is then cooled again from the outside with water and ice, and 40 g of ice are added. The compound obtained is decomposed by a solution of 12 ml of hydrochloric acid in 12 ml of water.

If the hydrochloric acid used is of a higher concentration, diphenylcarbinol may be dehydrated with the formation of dibenzhydryl ether:



The two layers obtained, i.e., the upper ethereal layer and the lower water layer, are separated in a separatory funnel. Two ethereal extracts (20 ml each) are made from the water layer.

To remove unreacted benzaldehyde, the combined ethereal extracts are washed with 10 ml of a 40 per cent sodium bisulphite solution. They are then washed with a sodium bicarbonate solution to remove sulphurous acid traces, and dried with anhydrous calcium chloride. Then, the ether is driven off in a water bath (apparatus 2):



A small residue of the ethereal solution is transferred to a porcelain dish. When the ether evaporates, a solid mass of diphenylcarbinol is formed.

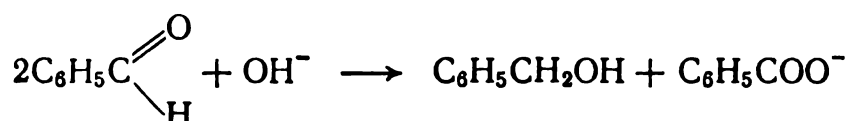
If diphenylcarbinol does not solidify, but remains as heavy oil due to impurities, it should be placed in a flask and the impurities should be steam distilled. The diphenylcarbinol which remains in the distilling flask solidifies when it cools. It is filtered off and recrystallized from ligroin or a mixture of gasoline and petroleum ether (1 : 1 by volume). The diphenylcarbinol yield is about 15 g.

Diphenylcarbinol (benzhydrol) is a colourless crystalline substance which melts at 68°C.

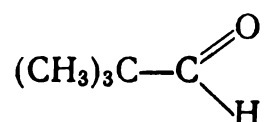
Chapter 17

CANNIZZARO REACTION

In 1853, Cannizzaro ascertained that aromatic aldehydes undergo redox conversion (disproportionation) under the action of a concentrated alkaline solution. An example of this reaction is the disproportionation of benzaldehyde into benzyl alcohol and benzoic acid:

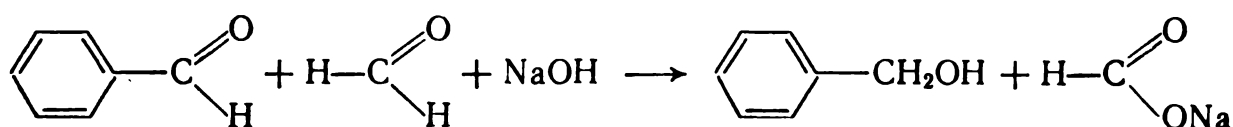


The reagents which enter into the Cannizzaro reaction, besides aromatic aldehydes, are formaldehyde and the aldehydes whose carbonyl group is bonded with the tertiary carbon atom, e.g.,



Most aldehydes of the fatty series do not enter into this reaction because, in a slightly alkaline medium, they condense like aldols.

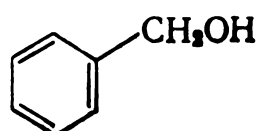
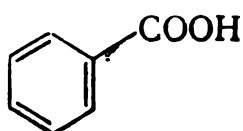
The "cross" Cannizzaro reaction is widely used. In it, aromatic and heterocyclic aldehydes are reduced to the appropriate alcohol under the action of formaldehyde, which is oxidized to formic acid:



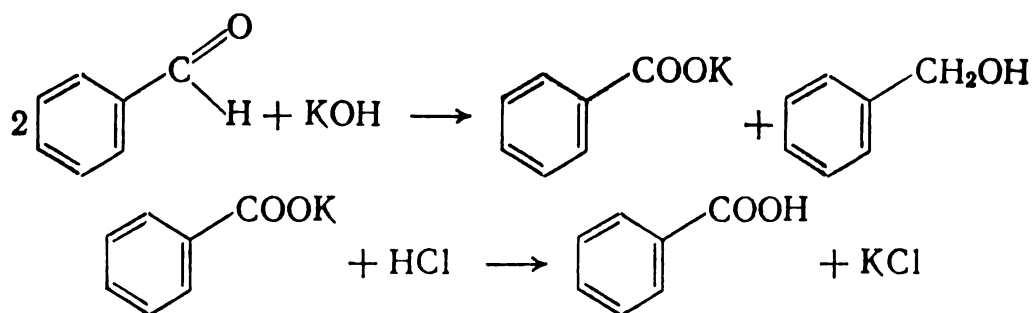
This reaction is used for reducing a large number of various aldehydes. For instance, the reaction can be used for obtaining furfuryl alcohol from furfural.

17.1. SYNTHESIS OF BENZOIC ACID AND BENZYL ALCOHOL

Formulas:



Main reactions:

**Reagents and Equipment**

Benzaldehyde	20 g (ca. 0.2 mole)	Reagent bottle or flat-bottom flask (100 ml)	1
Potassium hydroxide	18 g	Condenser, air	1
Ethyl ether	45 ml	Funnel, separatory	1
Sodium bisulphite, 40 per cent solution	10 ml	Flasks, Würtz (100 ml) . . .	2
Sodium carbonate		Condenser, Liebig	1
Sodium sulphate, anhydrous		Thermometer	1
Hydrochloric acid		Adapter, bent	1
		Receivers	2
		Flask, Bunsen	1
		Funnel, Büchner	1
		Flask, safety	1

Assembly

1. A 100-ml Würtz flask, placed in a water bath, is connected to a thermometer and to a Liebig condenser with a bent adapter, which is put into a receiver.

2. A 100-ml Würtz flask is fitted with a thermometer and an air condenser which is put into a receiver.

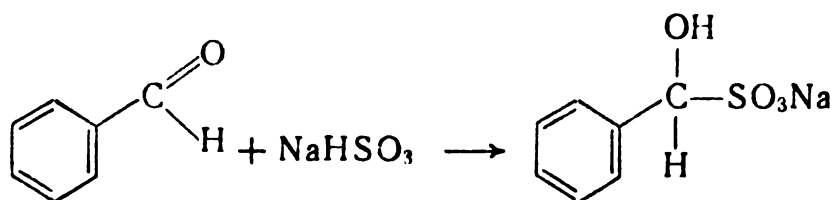
3. Suction apparatus (Fig. 2.21).

Procedure

Twenty grams of freshly distilled benzaldehyde are put in the 100-ml flat-bottom flask or a 100-ml reagent bottle and a cold solution of 18 g of potassium hydroxide in 12 ml of water is added while cooling the flask (or the bottle). The flask is then closed with a stopper having a side slit and its contents are shaken vigorously until a stable emulsion is formed. The mixture is allowed to stand for 10-12 hours. A small amount of water (needed for dissolving the crystals formed) is then added to a mixture of the benzyl alcohol and a crystalline mass of potassium benzoate. This solution is poured into a separatory funnel. A large amount of water should not be used because benzyl alcohol partially dissolves in water (4 g of it dissolve in 100 ml of water at 17°C). Benzyl alcohol is extracted from the solution by ethyl ether, making

2-3 ethereal extracts (15 ml each). The ethereal extracts are combined and shaken, twice adding 5 ml of a 40 per cent sodium bisulphite solution.

The ethereal extracts are treated with a concentrated sodium bisulphite solution so as to remove unreacted benzaldehyde, which forms a bisulphite derivative that does not dissolve in ether:



The ethereal layer is then washed with a sodium carbonate solution so as to free it from the sulphurous acid which may be present in a sodium bisulphite solution. When the organic layer has been poured from the separatory funnel into the flask, it is dried with anhydrous sodium sulphate or anhydrous potassium carbonate. The dried ethereal solution is poured into the 100-ml Würtz flask and the ether is thoroughly driven off in a water bath (apparatus 1). Then, benzyl alcohol is distilled off (apparatus 2) by heating the flask with either a burner flame through an asbestos gauze or a small, smoky flame. The fraction which boils at 204-206 °C is collected. The benzyl alcohol yield is about eight grams.

Benzyl alcohol (phenylcarbinol) is a colourless liquid with a faint, pleasant odour. It dissolves sparingly in water and well in alcohol, chloroform and ethyl ether. Its molecular weight is 108.13; b.p., 205.8 °C at 750 mm Hg or 93 °C at 10 mm Hg; m.p., -15.3 °C; d_4^{20} , 1.0455; and n_D^{20} , 1.5396. It is used as a lacquer solvent, and is also employed in perfumery.

When the aqueous alkaline solution is poured out of the separatory funnel after extraction with ether, it is acidified with hydrochloric acid. The benzoic acid which has precipitated is sucked off in the Büchner funnel and dried. To obtain benzoic acid of higher purity, it is recrystallized from boiling water. The benzoic acid yield is about nine grams.

Benzoic acid consists of colourless, lustrous leaflets which dissolve sparingly in cold water, better in hot water (0.2 g of it dissolves in 100 ml of water at 17 °C, or 2.2 g of it, at 75 °C) and well in chloroform, acetone, carbon tetrachloride, benzene and methyl alcohol. Its molecular weight is 122.05; b.p., 250 °C; m.p., 122.3 °C, and d_4^{15} , 1.2659.

Benzoic acid and its derivatives are widely used for synthesizing dyes and pharmaceuticals, and are also widely employed in the food industry.

Characterization Tests for Benzyl Alcohol. 1. Benzoic acid is formed when benzyl alcohol is oxidized with a chromic acid mixture or potassium permanganate.

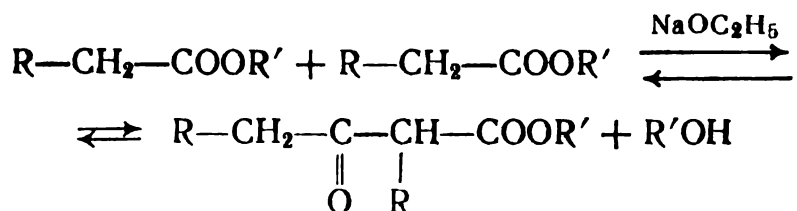
2. When a drop of benzyl alcohol is added to 2 ml of dilute nitric acid and the test tube is immersed in boiling water, a yellowish emulsion is formed and a strong benzaldehyde odour is given off.

Characterization Test for Benzoic Acid. A drop each of a 0.3 per cent hydrogen peroxide solution and of a ferric chloride solution are added to 1 ml of a benzoic acid solution. The test tube containing this mixture is immersed in boiling water. A red-violet colour appears as a result of the formation of salicylic acid.

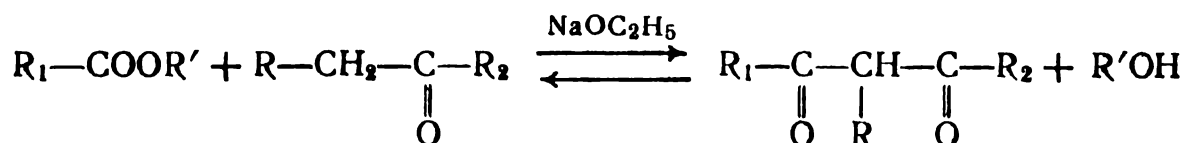
Chapter 18

CLAISEN REACTION

The Claisen reaction is of the aldol type. It consists in the condensation of esters with compounds which contain an active methylene group (esters, ketones and nitriles) in the presence of basic catalysts (metallic sodium, sodium amide and some organo-magnesium compounds). For instance, β -keto esters are formed when esters condense:



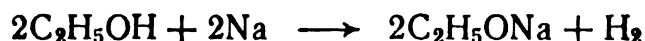
β -Diketones are formed when esters condense with ketones:



Whenever β -keto esters and β -diketones are being obtained, it is necessary to use pure anhydrous original substances and thoroughly dried equipment that is protected from moisture.

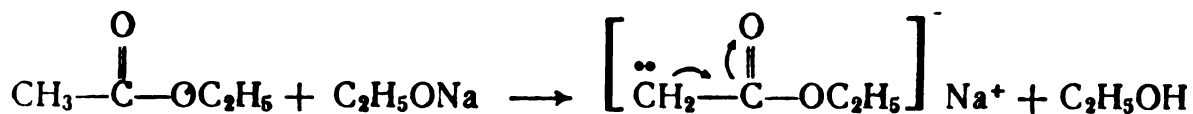
A classical example of ester condensation is the synthesis of ethyl acetoacetate (acetoacetic ester) from ethyl acetate in the presence of either metallic sodium or sodium ethoxide.

It has now been ascertained that the condensing agent is not metallic sodium, but sodium alkoxide (sodium ethoxide when ethyl acetoacetate is being obtained). Metallic sodium which is introduced into a reaction interacts with ethyl alcohol, whose traces are always present in ethyl acetate. The ethyl alcohol formed in the reaction gradually dissolves sodium; therefore, sodium ethoxide is continuously formed as the reaction occurs:

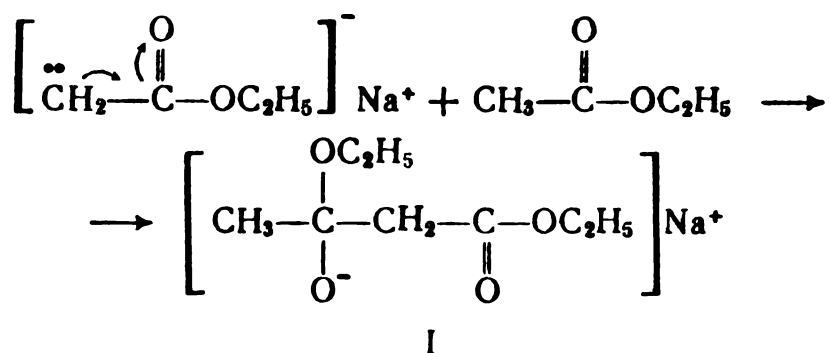


However, it is harmful to have a large amount of ethyl alcohol in ethyl acetate because ester condensation is reversible: under the action of ethyl alcohol and sodium ethoxide, ethyl acetoacetate decomposes into two molecules of the original ester.

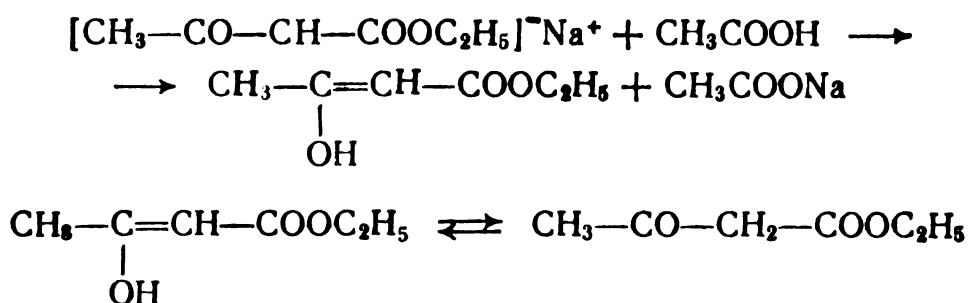
Sodium ethyl acetate is formed under the action of sodium ethoxide:



The compound obtained reacts with another molecule of ethyl acetate, forming complex I:



Complex I eliminates the molecule $\text{C}_2\text{H}_5\text{OH}$, forming the sodium ester $[\text{CH}_3\text{COCHCOOC}_2\text{H}_5]^- \text{Na}^+$. When acetic acid acts on it, a free enol form of ethyl acetoacetate originates and converts into the keto form until equilibrium is attained:



Similarly, β -diketones are obtained when esters condense with ketones.

An example of this type of condensation is the synthesis of benzoylacetone from acetophenone under the action of metallic sodium.

The solvent commonly used in ester condensation is excess ester, but ethyl ether, benzene or toluene is also occasionally employed.

In the synthesis of ethyl acetoacetate, excess ethyl acetate not only acts as a solvent, but also hinders the formation of the by-products, α -diketone and acyloin which may be formed in the presence of large amounts of sodium.

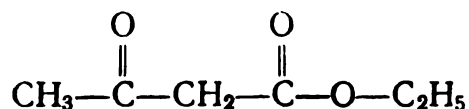
Ester condensation, very diverse and widespread, is a particular instance of the condensation reaction.

Many organic compounds, both synthetic and natural, are the result of condensation.

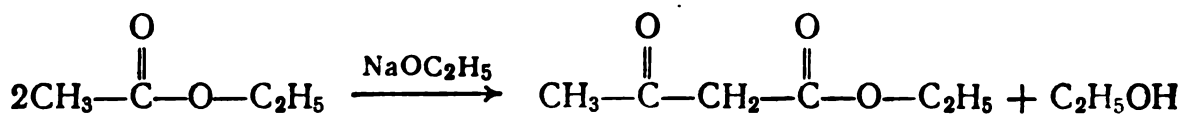
18.1. SYNTHESSES

ETHYL ACETOACETATE

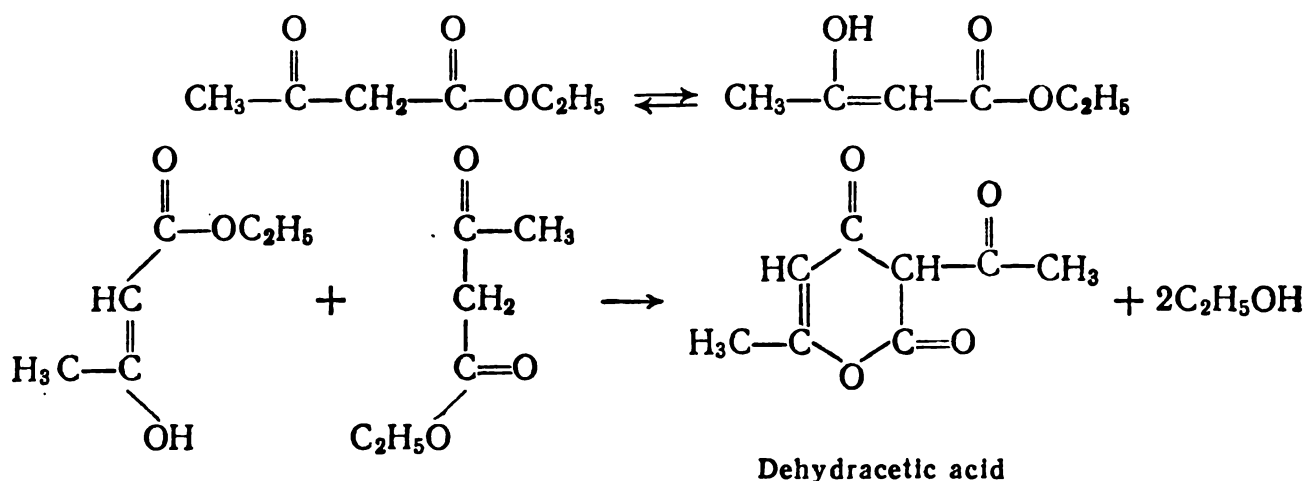
Formula:



Main reaction (see p. 294):



Side reactions:



Dehydracetic acid

Reagents and Equipment

Ethyl acetate	50 g or 56 ml (0.57 mole)	Flask, round-bottom (250 ml)	1
Sodium, metallic	5 g (0.22 gram atom)	Head, still	1
Acetic acid, 50 per cent	30 ml	Condenser, Liebig	1
Sodium chloride		Tube, calcium chloride	1
Sodium bicarbonate		Thermometer	1
Calcium chloride, anhy-		Funnel, separatory	1
drous		Flask, Würtz (100 ml)	1
		Adapter, bent	1
		Receivers	2
		Apparatus, vacuum distilla-	
		tion	1

Assembly

1. A still head connected to an inclined reflux condenser is put in the 250-ml round-bottom flask. The upper end of the condenser is closed with a calcium chloride tube. The straight neck of the still head is stoppered, and the flask is put in a sand bath. The apparatus and the original products must be thoroughly dried.

2. The 100-ml Würtz flask is fitted with a thermometer and a Liebig condenser having a bent adapter whose end is put into a receiver.

3. Vacuum distillation apparatus (see Fig. 3.9).

Procedure

Fifty-six millilitres of ethyl acetate are put in the dry, 250-ml round-bottom flask (apparatus 1), and five grams of finely threaded metallic sodium are added through the other opening of the still head by slightly removing the stopper. Hydrogen gradually begins to be faintly liberated. Somewhat later, the liquid boils moderately.

1. Ethyl acetate must not contain moisture, but it may contain 2-3 per cent of alcohol. If there is a small amount of alcohol in ether, the reaction occurs slowly; if there is a great deal of it, the ethyl acetoacetate yield decreases. Ethyl acetate is dried over calcium chloride and distilled. It must be worked with carefully because *ethyl acetate is flammable and forms explosive mixtures with the air.*

2. All safety precautions must be taken when working with metallic sodium. Safety glasses must be worn when cutting it. Large amounts of sodium must not be introduced into a reaction. Otherwise, by-products (α -diketone and acyloin) may be formed.

When the reaction slows down, the flask is heated for two or three hours in a sand bath while seeing that the mixture boils slightly. When only a few pieces of sodium remain in the flask, they should be converted into ethoxide by adding 2-3 ml of ethyl alcohol. The coloured clear solution formed is acidified, while stirring, with 30 ml of 50 per cent acetic acid until the litmus shows an acid reaction.

When ethyl acetate contains a lot of moisture, a gelatinous mass (sodium hydroxide) is obtained.

To separate the reaction mixture into layers, an equal amount of a saturated sodium chloride solution is added. If a precipitate develops, it is dissolved, while stirring, with a small amount of water. Then, the upper layer, which consists of ethyl acetoacetate and ethyl acetate, is separated in a separatory funnel. This layer is then shaken together with a small amount of a sodium bicarbonate solution saturated in the cold. The organic solution which separates is dried over calcium chloride, and then excess ethyl acetate, which boils away up to 95°C, is driven off by carefully heating the flask in a sand bath (apparatus 2).

The residue in the flask is distilled under vacuum and the fraction which boils at 86-90°C at 30 mm Hg or 69-73°C at 12 mm Hg is collected. Dehydroacetic acid, which crystallizes on cooling, remains in the flask after ethyl acetoacetate has been driven off. The ethyl acetoacetate yield is about 11 g.

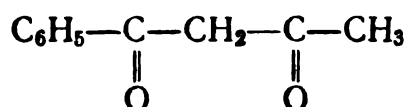
Ethyl acetoacetate is a colourless liquid with a refreshing odour. It dissolves poorly in water and mixes with organic solvents. Its molecular weight is 130.14; b.p., 181°C (dec.) at 760 mm Hg or 69-73°C at 12 mm Hg; m.p., -45°C; d_4^{20} , 1.023; and n_D^{20} , 1.4198. It is used for producing dyes and medicinals, and is also employed in syntheses.

Characterization Test. Ethyl acetoacetate with an aqueous ferric chloride solution produces a red-violet colour.

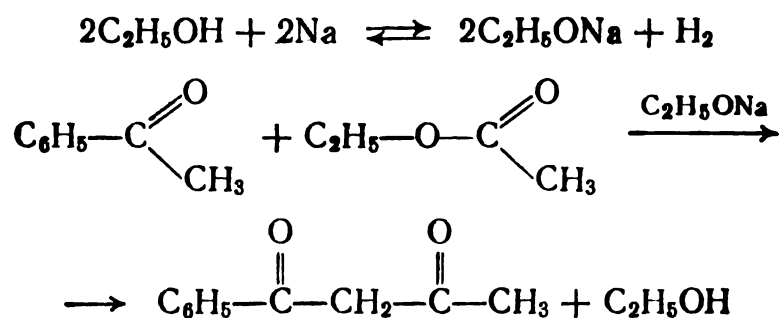
Ethyl acetoacetate consists of 93 per cent of the keto form and 7 per cent of the enol form. The presence of the enol form can be detected by a characteristic colour reaction with ferric chloride: a few drops of ethyl acetoacetate are dissolved in water; when 1-2 drops of a ferric chloride solution are added, a red-violet colour appears. If bromine water is added, the colour disappears because bromine reacts with the enol form of ethyl acetoacetate. The colour will appear somewhat later, however, since the free enol form gradually originates from the keto form of ethyl acetoacetate until equilibrium is attained.

BENZOYLACETONE

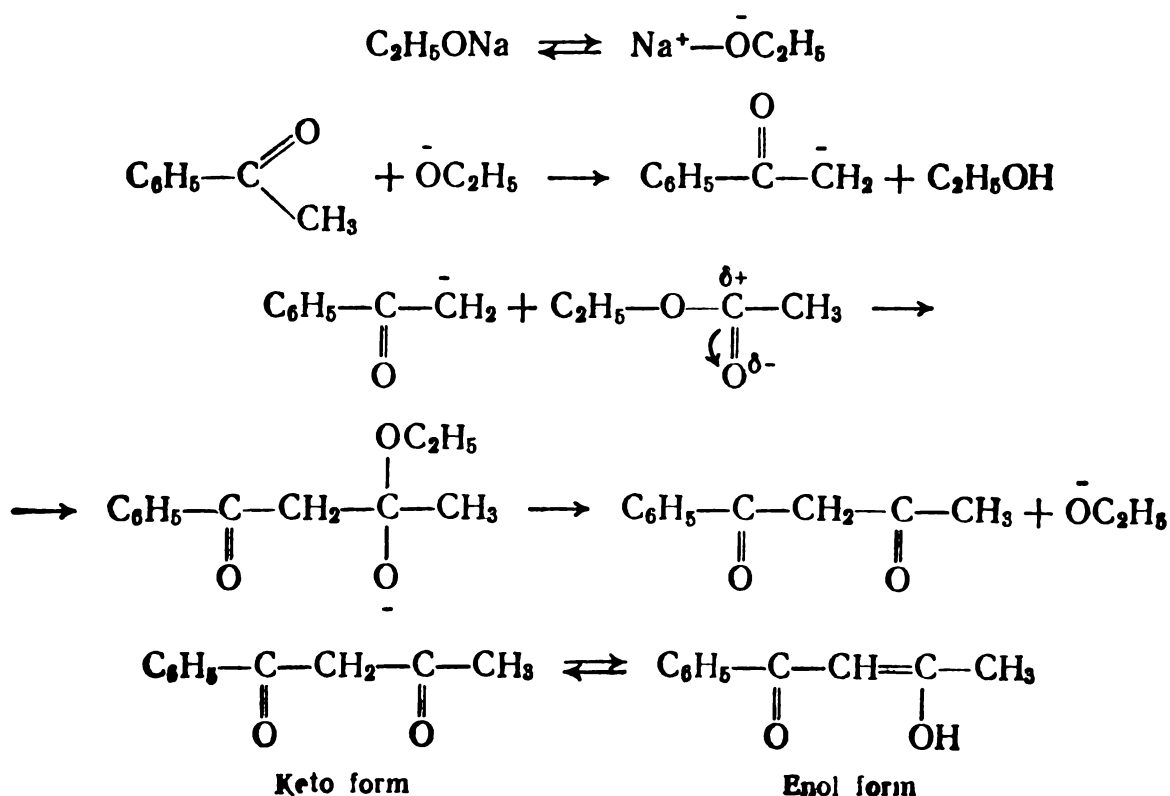
Formula:



Main reactions:



Reaction mechanism:



Reagents and Equipment

Ethyl acetoacetate . . .	18 g or 20.0 ml (0.2 mole)	Flask, round-bottom (250 ml)	1
Acetophenone	10 g or 9.7 ml (0.08 mole)	Condenser, Liebig	1
Sodium, metallic	2 g (0.09 gram atom)	Tube, calcium chloride . . .	1
Absolute ether	60 ml	Funnel, Büchner	1
Acetic acid		Flask, Bunsen	1
		Flask, safety	1
		Beaker	1
		Desiccator	1

Assembly

1. The 250-ml round-bottom flask, placed in a water bath, is connected to a reflux condenser, whose upper end is closed with a calcium chloride tube.

2. Suction apparatus (see Fig. 2.21).

Procedure

Ten grams of acetophenone, 18 g of ethyl acetate and 60 ml of absolute ether are put in the 250-ml round-bottom flask (see Chapter 2), and finely cut metallic sodium is added.

Acetophenone is a soporific. Its vapours must not be inhaled while working with it.

Ethyl acetate acts narcotically and irritates the mucous membranes.

The ether boils somewhat later. When the ether begins to boil more slowly, the flask is heated for 45 min in a water bath (apparatus 1).

After the reaction, the reaction mixture is cooled. The sodium benzoylacetone formed is sucked off in the Büchner funnel and then washed with dry ether and pressed between sheets of filter paper. Sodium benzoylacetone is then dissolved in 100 ml of water and filtered off. The solution is acidified with acetic acid while simultaneously cooling it with ice, and benzoylacetone is precipitated. The crystals formed are sucked off, washed with water and dried in a desiccator. The benzoylacetone yield is about eight grams.

Benzoylacetone (1-phenyl-1,3-butanedione) consists of strong-smelling crystals that dissolve well in alcohol and ether. Its molecular weight is 162.19; b.p., 261-262 °C at 760 mm Hg or 134-136 °C at 16 mm Hg; m.p., 61 °C, and $d_4^{20.5}$, 1.044. It is used in perfumery.

Characterization Test. Benzoylacetone with an aqueous ferric chloride solution produces a red colour.

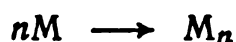
Chapter 19

POLYMERIZATION AND POLYCONDENSATION REACTIONS

Synthetic high-molecular-weight compounds are obtained as a result of two types of reactions: polymerization and polycondensation. These reactions are of great technical importance. They are used for obtaining synthetic resins, fibres and rubber, which are widely employed in the national economy.

19.1. POLYMERIZATION

Polymerization is the joining together of many small molecules to form very large molecules:



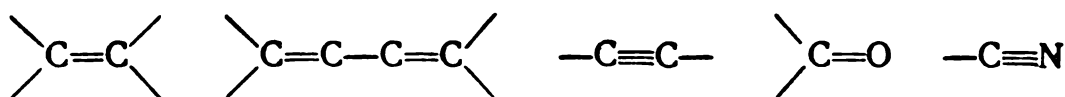
where M = monomeric molecule;

M_n = macromolecule consisting of n monomeric units;

n = degree of polymerization.

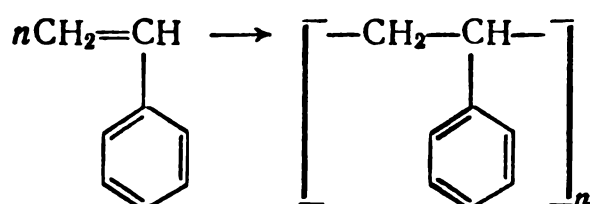
Monomeric molecules in the composition of macromolecules are monomeric units. The elementary composition of macromolecules (without taking the terminal groups into account) does not differ from the composition of a monomer.

Many known compounds with multiple bonds tend to undergo polymerization, which occurs due to the saturation of valencies of the initial monomeric molecules which results either from the rupture of their multiple bond



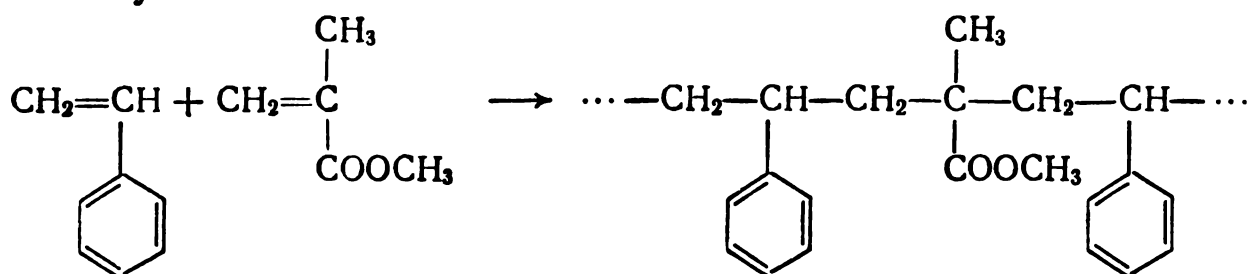
or, in three-membered cyclic oxides, from the opening of the ring.

Polymerization involving the molecules of one substance is called *homopolymerization*, e.g., styrene polymerization:

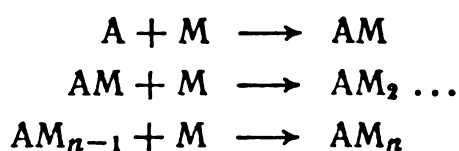


If polymerization involves various monomers, it is called *copolymerization*, e.g., the copolymerization of styrene and methyl

methacrylate:



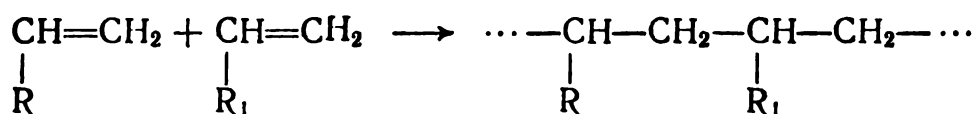
The stages which polymerization necessarily undergoes are the initiation and the propagation of macromolecules. In initiation, active particles (A) originate in a system. They are capable of initiating the propagation reaction with the subsequent addition of monomeric molecules to the active particle:



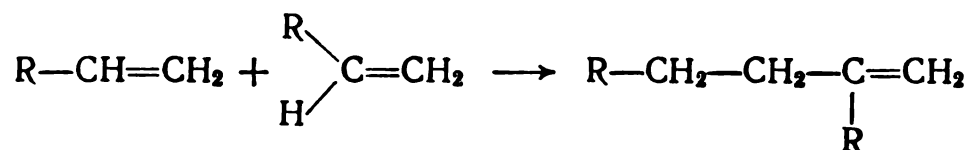
The polymerization mechanism is determined by the chemical nature of the particles of the AM_n type. These particles are the intermediates of polymerization.

There are two main types of polymerization: chain and step reactions.

Chain-reaction Polymerization. In this case, the original polymerization products are not stable molecules and cannot be isolated. The reaction products are high-molecular-weight substances:



Step-reaction Polymerization. The reaction products can be isolated at different stages of the process:

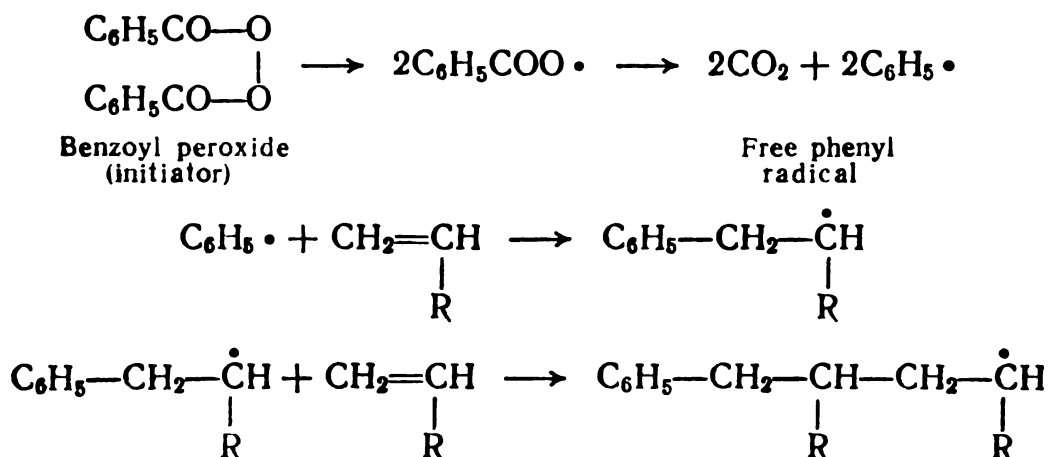


Polymerization can be either free-radical or ionic, depending on the reaction mechanism.

Free-radical polymerization is initiated by substances capable of decomposing to free radicals (peroxides, persulphates, diazo and azo compounds, etc.) under reaction conditions as well as by the action of heat and light.

The radicals of initiators are in the composition of a polymeric molecule, constituting its terminal group. A chain is terminated when the molecule of a propagating polymer collides either with the monomeric molecule or with the molecule of the chain propa-

gation controller, which is specially added. Chain polymerization occurs according to this mechanism:



Ionic polymerization occurs owing to the formation of reactive ions from monomeric molecules in the presence of catalysts (acids, anhydrous chlorides of aluminium, boron, etc.). The catalyst is reactivated during ionic polymerization and does not enter into the composition of a polymer. Ionic polymerization can occur by either the chain-or step-reaction mechanism.

There are several methods of polymerization: block, solution and emulsion. A variety of emulsion polymerization is suspension polymerization.

Block polymerization is the polymerization of a monomer without a solvent. If the reaction is carried out until a monomer is completely converted, a monolith (block) is obtained. The monolith has the shape of the vessel into which the original monomer was poured. In this case, both the initiators of free-radical polymerization and the monomer-soluble catalysts of ionic polymerization can be used. The difficulty of this method is that heat liberated in the reaction must be rapidly withdrawn.

Solution polymerization occurs either in a medium which dissolves only the monomer or in a liquid which mixes with a monomer and also with the polymer being formed (lacquer technique). In the former case, the polymer being formed precipitates and can be filtered off. In this method, free-radical initiators and ionic-polymerization catalysts which dissolve in the reaction medium are used. The advantage of this method is that heat can be easily withdrawn; its disadvantage is that the polymer is removed from the solvent with difficulty and must be granulated.

Emulsion polymerization is the most commonly used industrial method for obtaining polymers. In it, polymerization is carried out in a liquid medium (in most cases, water) that dissolves neither the monomer nor the polymer. To stabilize the emulsion, it is necessary to use soaps (oleates, palmitates, sodium sulphonates of the aromatic and high-molecular-weight fatty series, etc.) as well as polyvinyl alcohol, carboxymethylcellulose and some other sub-

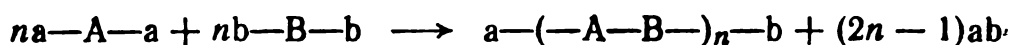
stances. In this polymerization method, water-soluble low-temperature initiators are usually employed. Besides initiators, buffers (bicarbonates, phosphates and alkaline acetates), which act as regulators, are introduced into the system so as to maintain the pH of the medium at a constant level. In emulsion polymerization, the polymer is in the form of a latex with the particle size of about 10^{-4} cm. The advantage of this method is that heat is easily withdrawn and a high-molecular-weight product is readily obtained; its disadvantage is that the emulsifier must be washed away from the polymer.

Suspension polymerization occurs in the presence of an emulsifier and an initiator. The polymer is in the form of minute granules. The disadvantage of this polymerization method is that the stabilizer must be washed away from the polymer.

On heating, a process opposite to polymerization often occurs. It is called *depolymerization*. Some cyclic dimers, whose rings consist only of carbon atoms, depolymerize very readily. However, most of the other dimers and polymers depolymerize only under very severe conditions.

19.2. POLYCONDENSATION (CONDENSATION POLYMERIZATION)

Polycondensation is a process in which high-molecular-weight compounds are formed with the simultaneous isolation of a low-molecular-weight product (water, hydrogen halide, ammonia, alcohol, etc.):



where a and b are functional groups (OH, COOH, NH₂, etc.).

Unlike the polymerization products, the composition of the elementary unit of the polymer obtained as a result of polycondensation does not conform to the elementary composition of the original monomer.

The polycondensation reaction depends on the chemical structure both of the original substances and of the products being obtained, their physical properties, the nature of the by-products, and the reaction rate constants. Polycondensation can occur only when the original substances have at least two functional groups which can participate in a reaction.

A thermoplastic, fusible linear polymer which dissolves in organic solvents is obtained in a reaction if the original monomer has two functional groups. If even one of the initial reagents has three or more functional groups, an infusible stereospecific polymer which does not dissolve in organic solvents is formed. Therefore,

polycondensation in which stereospecific polymers may be formed should be carried out in such a way as to prevent the product from solidifying in the reaction vessel. To obtain a solid resin, the liquid resin is poured into moulds from which a solidified polymer can be easily withdrawn.

In polycondensation, a reverse process, i.e., degradation, occurs simultaneously with polymer chain propagation. Degradation can be reduced by thoroughly removing low-molecular-weight compounds from the reaction sphere in conformity with the law of mass action.

The polycondensation reaction rate can be controlled by changing the temperature of the reaction medium. For instance, to retard the reaction, the reaction vessel in which the process is occurring must be cooled.

A few types of polycondensation reactions are given below.

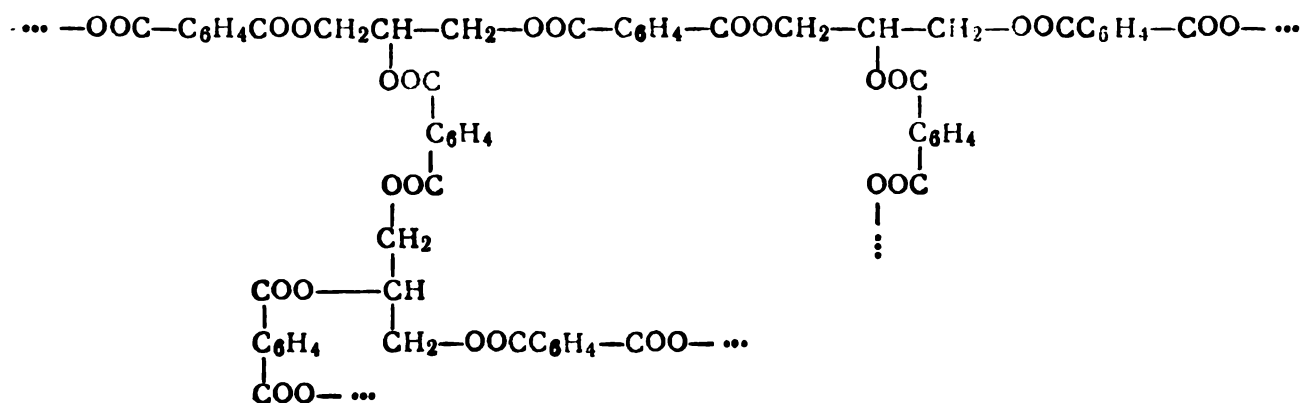
Polycondensation of Polybasic Acids with Polyhydric Alcohols.

High-molecular-weight polyester resins are obtained when polybasic carboxylic acids are polycondensed together with polyhydric alcohols. The most commonly known polymer of this group is the glyptal resin, obtained by polycondensing phthalic acid (or its anhydride) with glycerol.

Polyesters with different properties can be obtained, depending on the ratio of the components and the reaction conditions. At 150 °C, for instance, phthalic anhydride, after interacting with glycerol, at first forms a linear polyester

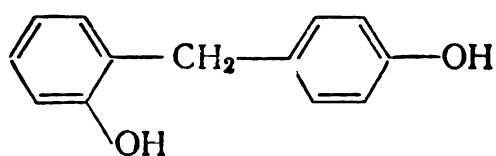


which is a soft fusible resin that dissolves in alcohol, acetone and chloroform. At this temperature, only the primary alcoholic groups of glycerol interact with phthalic anhydride. The secondary ones remain free. When these polyesters are heated further (up to 220 °C) and phthalic anhydride is in excess, they gradually cross-link. Crosslinking occurs by means of the secondary alcoholic groups of glycerol and the carboxyl groups of the linear polyesters which have already been formed. In this case, water is eliminated and a three-dimensional rigid structure of the glyptal resin is obtained:

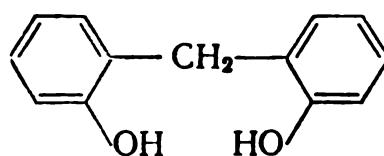


A stereospecific polymer neither dissolves in acetone nor melts, but it can be moulded well. It is very hard, mechanically strong, and resistant to the action of water.

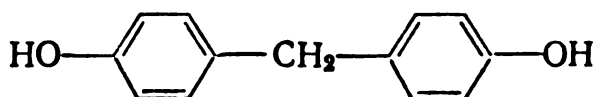
Polycondensation of Phenols with Aldehydes. The reaction between phenols and aldehydes occurs on heating in the presence of catalysts (acids or alkalis). For instance, when phenol-formaldehyde resins are being obtained, isomeric dihydroxydiphenylmethanes are formed at the initial stage of polycondensing phenol with formaldehyde in the presence of acids



2,4'-Dihydroxydiphenylmethane

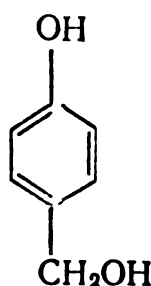
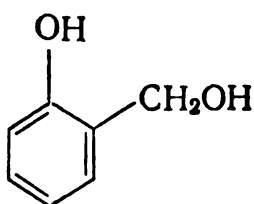


2,2'-Dihydroxydiphenylmethane



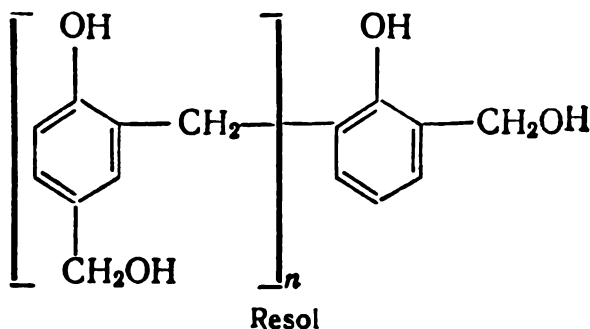
4,4'-Dihydroxydiphenylmethane

while *o*- and *p*-hydroxybenzyl alcohols are formed in the presence of alkali:



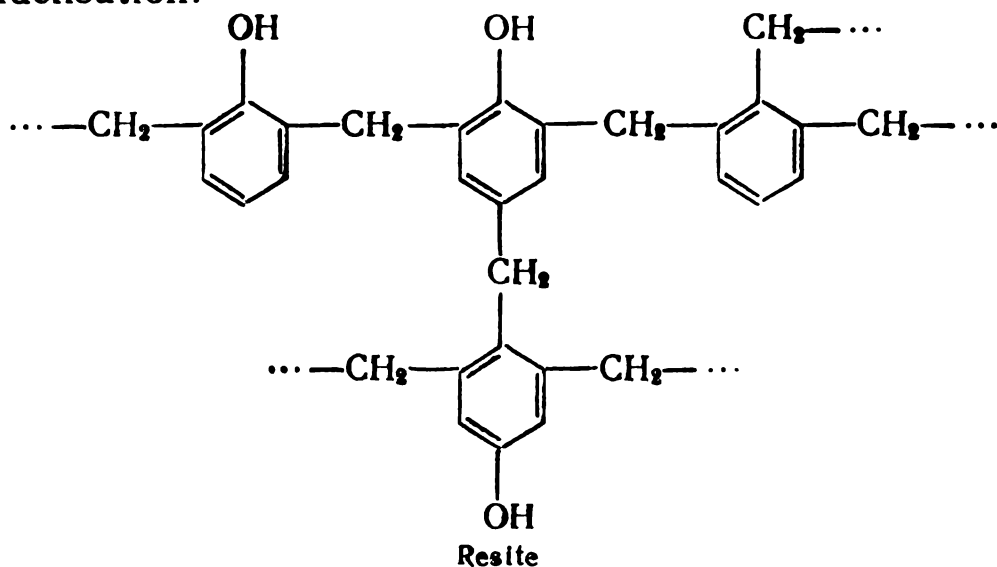
When heated further, these intermediate reaction products turn into resins.

In an alkaline medium and in excess formaldehyde, the initial polycondensation product, resol, is a fusible substance which dissolves in organic solvents:



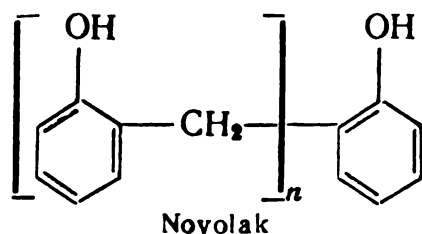
When resol is heated, it passes through an intermediate called resitol, which neither melts nor dissolves but swells, into resite, which is an infusible, insoluble and non-swelling end product of

polycondensation:



At the resite stage, phenol-formaldehyde resins have a three-dimensional structure and are used in technological processes for producing moulded articles.

When phenol is polycondensed with formaldehyde in the presence of an acid catalyst and when phenol is in excess, novolak, i.e., a low-melting resin which dissolves in organic solvents, is obtained:



Acids, however, are used as catalysts only in instances when a resin does not solidify too quickly, since they greatly accelerate the polycondensation reaction.

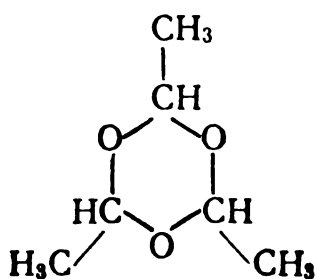
Polycondensation of Diamines and Dibasic Acid Chlorides. Polyamides are formed in this reaction. Strong elastic threads are made out of them after they have been appropriately treated. For instance, when hexamethylenediamine is polycondensed with the chloride of adipic acid, a polyamide called Nylon is formed:



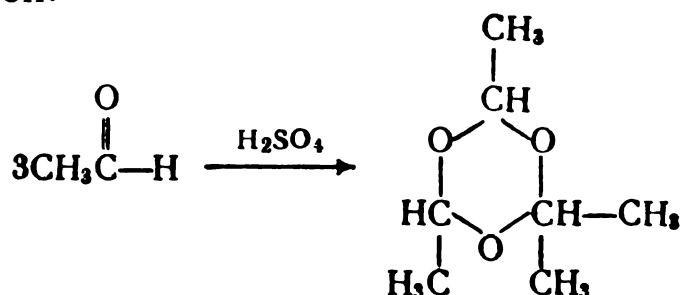
19.3. SYNTHESSES

PARALDEHYDE

Formula:



Main reaction:



Reagents and Equipment

Acetaldehyde	50 g or 64.0 ml (1.13 mole)	Flask, round-bottom (500 ml) . . .	1
Calcium chloride . . .	10 g	Funnel, separatory	1
Sulphuric acid		Condenser, Liebig	1
($d = 1.84$)	0.5 g or 0.3 ml	Flask, Würtz (50 ml)	1
Ice		Dephlegmator	1
		Thermometer	1
		Adapter, bent	1
		Receiver	1

Assembly

1. The 500-ml round-bottom flask is put in a water bath and fitted with a reflux condenser.

2. The 50-ml Würtz flask is fitted with a dephlegmator, which is connected to a thermometer and a Liebig condenser with a bent adapter whose end is put into a receiver.

Procedure

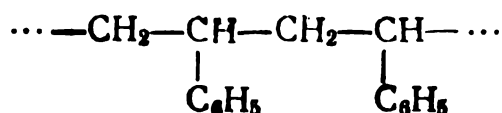
Sixty-four millilitres of freshly distilled acetaldehyde are put into the 500-ml round-bottom flask. The flask is cooled with water and ice, and 0.3 ml of sulphuric acid is added dropwise on the top through the condenser, which is intensively cooled with a strong jet of water. The mixture in the flask boils, since the polymerization reaction is exothermic. After the reaction, the contents of the flask are poured into a separatory funnel and then washed several times with water and dried over calcium chloride. Then, paraldehyde is driven off in apparatus 2 at 122-124 °C. The paraldehyde yield is about 37 g.

Paraldehyde is a liquid with a characteristic odour. It dissolves poorly in water and well in alcohol and ether.

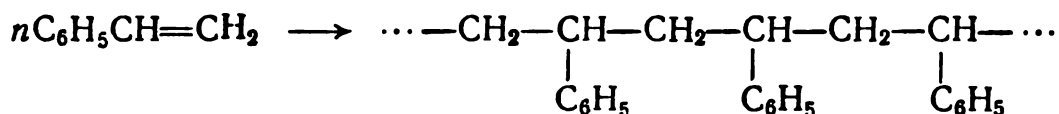
Characterization Test. When paraldehyde is heated in a water bath together with a small amount of sulphuric acid it depolymerizes to acetaldehyde.

POLYSTYRENE

Formula:



Main reaction:



Preparation of Polystyrene by the Suspension Polymerization of Styrene in the Presence of the Benzoyl Peroxide Initiator and the Polyvinyl Alcohol Emulsifier

Reagents and Equipment

Styrene	10 g or 11 ml (ca. 0.1 mole)	Reaction vessel with a side tube .	1
Benzoyl peroxide . .	0.2 g	Stirrer	1
Polyvinyl alcohol . .	0.234 g	Condenser, reflux	1
		Thermometer	1
		Funnel, Büchner	1
		Flask, Bunsen	1
		Flask, safety	1

Assembly

1. The reaction vessel is fitted with a mechanical stirrer and a reflux condenser and then placed in a water bath (Fig. 19.1), into which a thermometer is put.

2. Suction apparatus (see Fig. 2.21).

Procedure

A solution of 0.234 g of polyvinyl alcohol in 60 ml of water is poured into the reaction vessel, and a mixture of 10 g of freshly distilled styrene and 0.2 g of benzoyl peroxide is added.

Styrene may polymerize even at room temperature. Therefore, inhibitors (usually hydroquinone) are added to it when it is being stored or transported and are washed away before polymerization.

Caution: *Benzoyl peroxide is explosive!*

The reaction vessel is placed in a water bath and the stirrer is switched on. Polymerization is carried out for four or five hours at 80 °C, strictly maintaining this temperature and closely watching how the stirrer operates. Polymerization is stopped as soon as the polymeric granules solidify. The granules are then filtered off, washed with water and dried on filter paper.

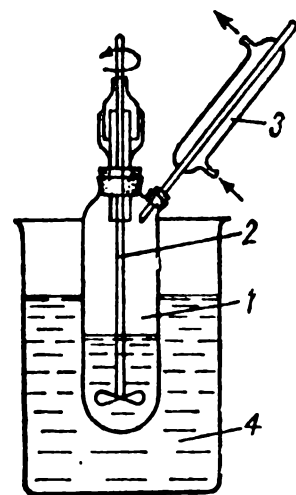


Fig. 19.1. Apparatus for suspension polymerization:

1—reaction vessel;
2—stirrer; 3—condenser; 4—water bath

Preparation of Polystyrene by Polymerizing Styrene in a Solvent in the Presence of the Benzoyl Peroxide Initiator

Reagents and Equipment

Styrene	20 g or 2.2 ml (ca. 0.2 mole)	Flask, round-bottom (150 ml) . . .	1
Benzoyl peroxide . .	0.4 g	Condenser, Liebig	1
Benzene	20 g or 22.5 ml	Dish, porcelain	1
Petroleum ether		Thermometer	1

Assembly

The 150-ml round-bottom flask fitted with a reflux condenser is placed in a water bath, into which a thermometer is put.

Procedure

Twenty grams of freshly distilled styrene and 0.4 g of benzoyl peroxide are put in the 150-ml round-bottom flask. Next, 20 g of benzene are added. The flask is then heated for four hours (apparatus 1) at 90-95 °C. After polymerization, the contents of the flask are cooled and poured into a porcelain dish, and petroleum ether is added. The solvent is decanted and the polystyrene precipitate is put in a vacuum drier heated to 80 °C at 500-600 mm Hg.

Preparation of Polystyrene by Block Polymerization**Reagents and Equipment**

Styrene	5 g or 5.5 ml (ca. 0.05 mole)	Test tube (150×75 mm)	1
Benzoyl peroxide . .	0.05 g		

Procedure

Five grams of styrene are put in a wide test tube. Then, 0.05 g of benzoyl peroxide is added and the test tube is carefully heated for 1-1.5 h in a water bath. A glassy polymer is formed.

Caution: *Benzoyl peroxide is explosive!*

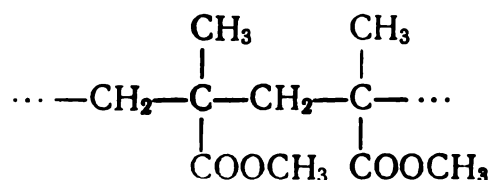
Polystyrene is readily flammable and burns with a bright smoky flame. It dissolves in dioxane, benzene and carbon tetrachloride, but does not dissolve in alcohol and ligroin. It swells in acetone. Its molecular weight is 30,000-100,000.

Polystyrene is employed as an electric insulator and as anticorrosive coating of both chemical equipment and accumulators. It is also used for making household articles and pharmaceutical vessels. Polystyrene lacquers are used as anticorrosive and electric insulating coating.

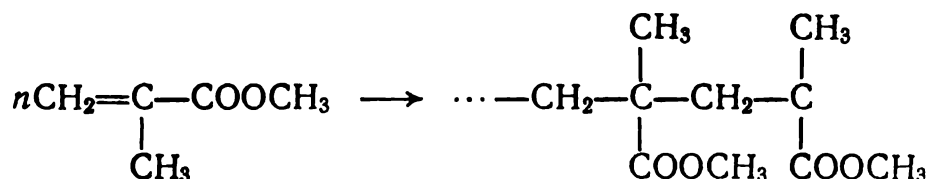
Characterization Test. When polystyrene is heated to 300 °C, it depolymerizes.

POLYMETHYL METHACRYLATE

Formula:



Main reaction:



*Preparation of Polymethyl Methacrylate
by Emulsion Polymerization in the Presence
of the Ammonium Persulphate Initiator*

Reagents and Equipment

Methyl methacrylate	10 g or 10.58 ml (ca. 0.1 mole)	Flask, round-bottom with 3 necks (250 ml)	1
Ammonium persulphate	1 g	Condenser, Liebig	1
		Funnel, dropping	1
		Stirrer, mechanical	1
		Thermometer	1
		Evaporator	1
		Flask, Bunsen	1
		Funnel, Büchner	1
		Flask, safety	1

Assembly

1. The 250-ml round-bottom flask with 3 necks, fitted with a reflux condenser, a mechanical stirrer and a dropping funnel, is placed in a water bath, into which a thermometer is put.

2. The 250-ml round-bottom flask with 3 necks, fitted with a mechanical stirrer and a reflux condenser, is connected to a steam generator by a gas inlet tube, which reaches the bottom of the flask.

3. Suction apparatus (see Fig. 2.21).

Procedure

One hundred millilitres of distilled water are poured into the 250-ml round-bottom flask with 3 necks (apparatus 1) and then one gram of ammonium persulphate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, is dissolved in the water. The flask is heated to 80°C in a water bath. Afterwards,

10 g of freshly distilled methyl methacrylate are added dropwise from a dropping funnel while maintaining that temperature and stirring vigorously. In 4-6 h, heating is stopped and vapour from the steam generator (apparatus 2) is passed into the emulsion until the polymer coagulates.

If the polymer does not precipitate, a small amount of either a 10 per cent sodium chloride solution or hydrochloric acid is added. The polymer precipitate is filtered off in the Büchner funnel, washed, and air-dried. If sodium chloride was used to coagulate the polymer, the polymer precipitate is washed until the test for the chloride ion is negative.

*Preparation of Polymethyl Methacrylate
by Suspension Polymerization in the Presence
of the Benzoyl Peroxide Initiator
and Buffer Emulsifiers*

Reagents and Equipment

Methyl methacrylate . .	50 g or 52.9 ml (ca. 0.5 mole)	Flask, round-bottom, with 3 necks (500 ml)	1
Disodium phosphate . .	0.85 g	Condenser	1
Monosodium phosphate	0.05 g	Stirrer, mechanical	1
Benzoyl peroxide . . .	1 g	Thermometer	1
Sodium polymethacrylate	1 g	Filter, glass, porous	1

Assembly

1. The 500-ml round-bottom flask with 3 necks, fitted with a reflux condenser, a thermometer and a mechanical stirrer, is placed in a water bath.

Procedure

A solution of one gram of sodium polymethacrylate in 150 ml of water is poured into the 500-ml round-bottom flask with 3 necks; then a buffer solution of 0.85 g of disodium phosphate and 0.05 g of sodium phosphate in 5 ml of water is added. Afterwards, a solution of one gram of benzoyl peroxide in 50 g of freshly distilled methyl methacrylate is poured in. The reaction is carried on for 45 min at 80-82 °C while continuously stirring the mixture.

The stirrer rotation rate controls the size of the drops and, accordingly, that of the granules. After the reaction, the granules obtained are filtered off in a glass porous filter and then washed with water and air dried.

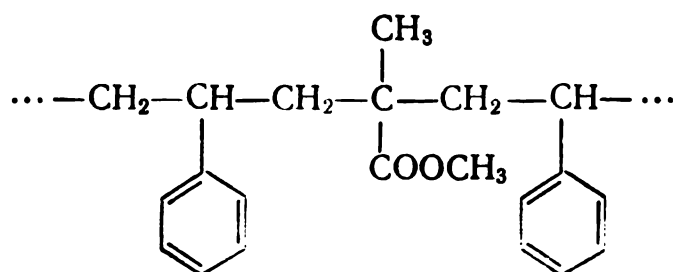
Polymethyl methacrylate (Plexiglas) dissolves in acetone, benzene, ethyl acetate, dioxane and acetic acid, but does not dissolve in gasoline, ether, ethyl alcohol, carbon tetrachloride and water. Its molecular weight is 100,000-200,000.

Articles are made out of polymethyl methacrylate by die casting and extrusion.

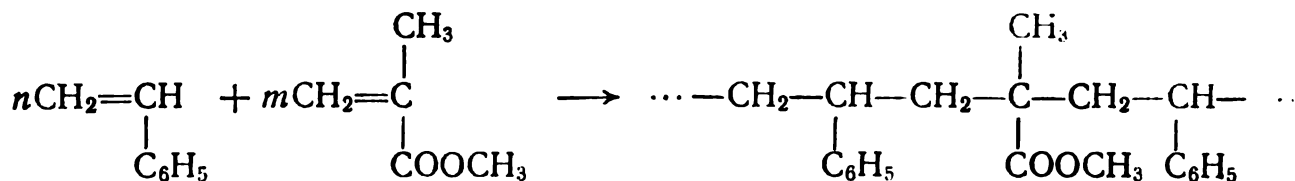
Characterization Test. When polymethyl methacrylate is heated to 100 °C, it begins to soften. At 250-300 °C, it almost completely depolymerizes.

COPOLYMER OF STYRENE WITH METHYL METHACRYLATE

Formula of the copolymer:



Main reaction:



Reagents and Equipment

Methyl methacrylate . . .	10 g or 10.58 ml (ca. 0.1 mole)	Flask, round-bottom, with 3 necks (500 ml)	1
Styrene	50 g or 55 ml (ca. 0.5 mole)	Condenser, Liebig	1
Ammonium persulphate	1.45 g	Funnel, dropping	1
Polyvinyl alcohol . . .	2 g	Stirrer, mechanical	1
Sodium chloride, 10 per cent solution	100 g	Thermometer	1
		Funnel, Büchner	1
		Flask, Bunsen	1
		Flask, safety	1

Assembly

1. The 500-ml round-bottom flask with 3 necks, fitted with a reflux condenser, a dropping funnel and a mechanical stirrer, is placed in a water bath into which a thermometer is put.

2. Suction apparatus (Fig. 2.21).

Procedure

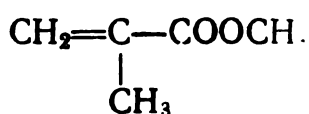
Two grams of polyvinyl alcohol and 240 ml of distilled water are put in the 500-ml round-bottom flask with 3 necks. Polyvinyl alcohol is introduced into the reaction as an emulsifier. Then,

1.45 g of ammonium persulphate (initiator) is put into the solution obtained. The contents of the flask are heated to 80°C, and a mixture of 50 g of styrene and 10 g of methyl methacrylate is added dropwise from a dropping funnel. The copolymerization reaction takes five hours. The emulsion obtained is then destroyed at that temperature, adding a 10 per cent sodium chloride solution until the copolymer precipitates completely. The emulsion can be destroyed also by treating it with steam.

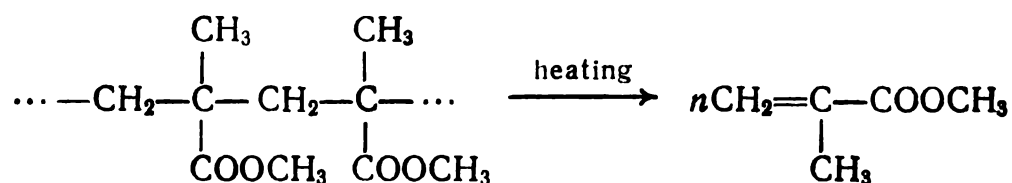
After standing, the copolymer is filtered off in a Büchner funnel and then washed with water and dried.

METHYL METHACRYLATE (FROM POLYMETHYL METHACRYLATE)*

Formula:



Main reaction:



Reagents and Equipment

Polymethyl methacrylate . . . 12.5 g	Flask, Würtz (50 ml) 1
	Condenser, Liebig 1
	Adapter, bent 1
	Receiver 1
	Thermometer 1

Assembly

1. The 50-ml Würtz flask is connected to a thermometer and a Liebig condenser with a bent adapter, whose end is put into a receiver cooled with water and ice.

Procedure

Ground polymethyl methacrylate weighing 12.5 g is put into the 50-ml Würtz flask (apparatus 1), which is heated with a small bright burner flame or in the Babo funnel. When the temperature is higher than 300°C, polymethyl methacrylate softens and depolymerizes into methyl methacrylate, which is distilled into the re-

* Preparation of a monomer from the scraps or waste of polymethyl methacrylate by depolymerization.

Assembly

1. A chemical beaker is placed in an oil bath into which a thermometer is put. The beaker should not touch the bottom of the bath.

Procedure

Since acrolein vapours are formed in the reaction, synthesis must be carried out in a fume cupboard.

Finely ground phthalic anhydride weighing 7.4 g, together with 3.1 g of glycerol, is put in the 50-ml beaker. The mixture is mixed thoroughly and carefully heated to 150-180 °C. Steam then comes out of the reaction mass. Next, the temperature is raised to 230 °C and the mixture is heated at this temperature for about 40 min until bulging occurs. After the reaction, the mass is poured into a flat tin vessel and ground. The glyptal resin yield is about eight grams.

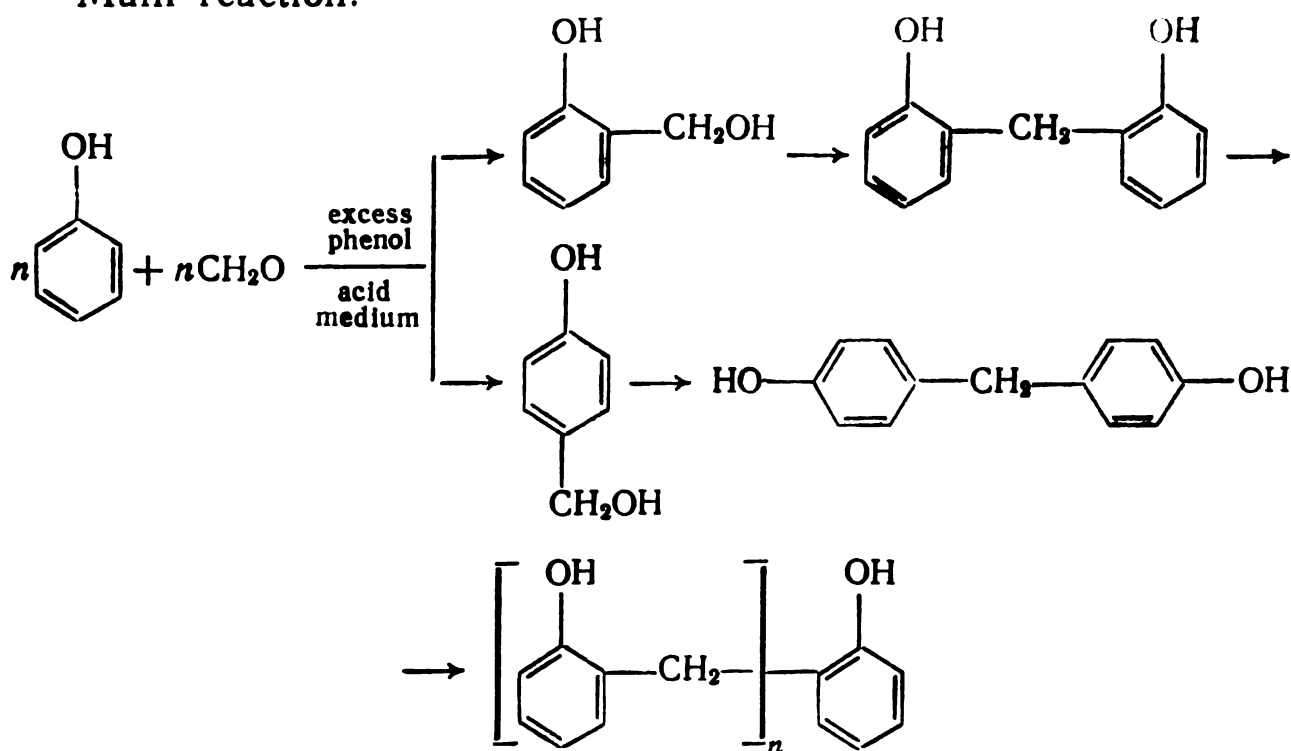
The glyptal resin is a colourless, solid brittle mass which is used for producing lacquers and enamels.

Characterization Test. When the glyptal resin is intensely heated, it decomposes, forming a white deposit of phthalic anhydride.

PHENOL-FORMALDEHYDE RESIN

Preparation of Novolak

Main reaction:



Reagents and Equipment

Phenol	38 g	Flask, round-bottom (300 ml) . . .	1
Formalin, 40 per cent	15 g or 15 ml	Condenser, Liebig	1
Hydrochloric acid		Thermometer	1
($d = 1.19$)	0.5 g or 0.42 ml	Test tubes	2
		Dish, porcelain	1

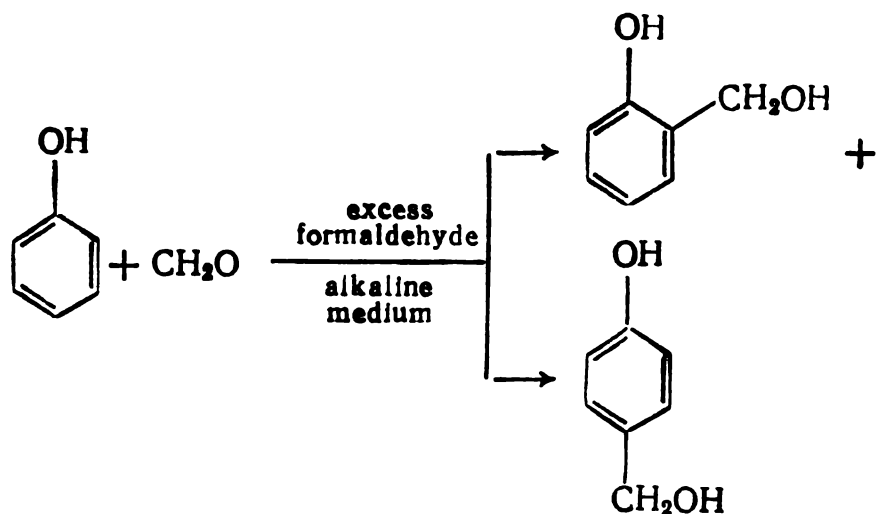
Assembly

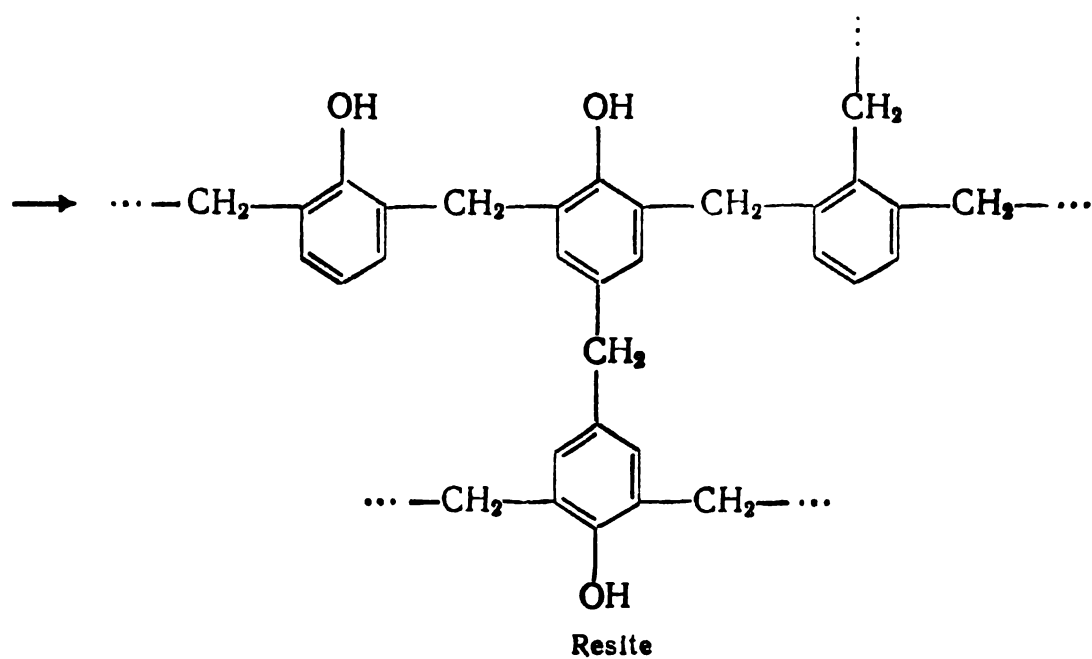
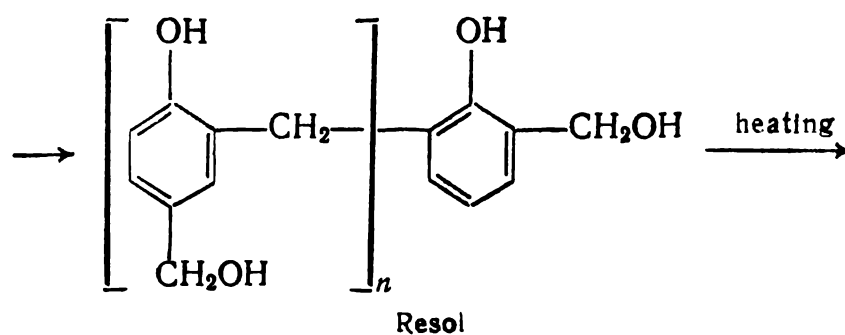
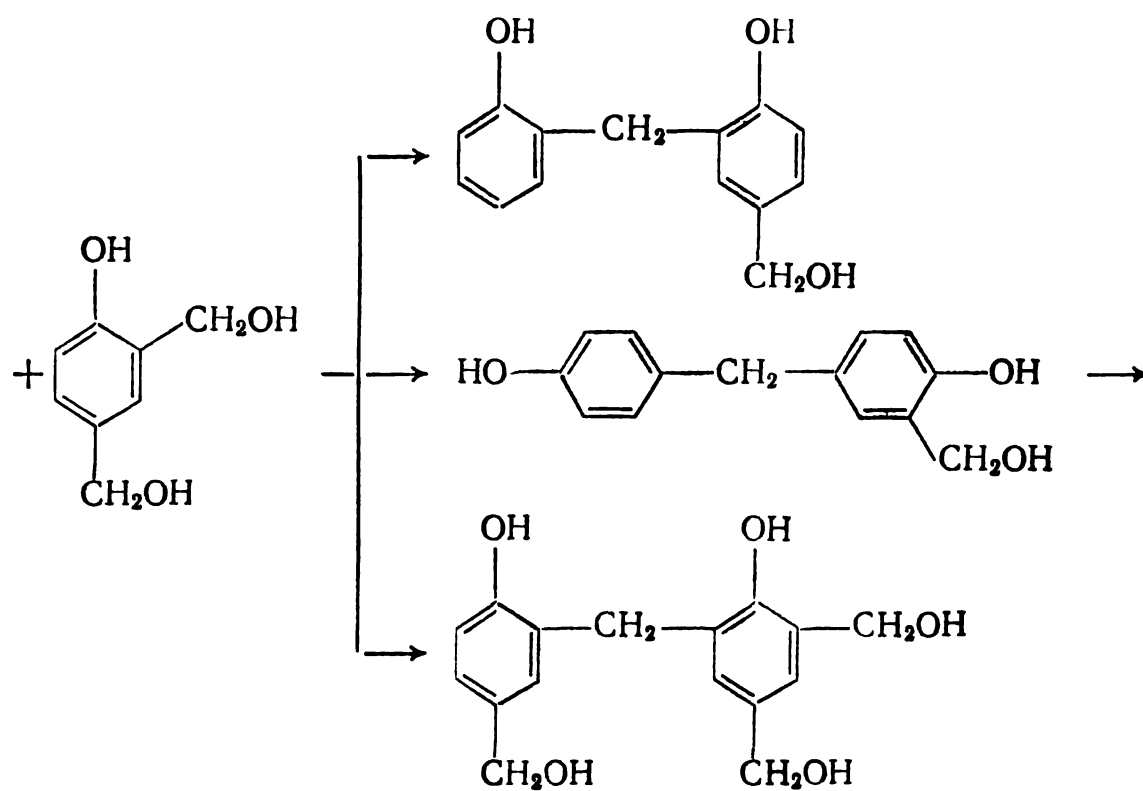
1. The 300-ml round-bottom flask is fitted with a reflux condenser and placed in a water bath into which a thermometer is put.

Procedure

Thirty-eight grams of phenol and 15 g of 40 per cent formalin are put in the 300-ml round-bottom flask. The mixture is then shaken until complete dissolution. Afterwards, 0.5 g of hydrochloric acid ($d = 1.19$) is added and the mixture is heated (apparatus 1) for 20-40 min at 90-100°C in a water bath in a fume cupboard. As soon as the reaction becomes vigorous, heating is stopped. The reaction continues spontaneously. When the reaction is no longer vigorous, heating is continued until the mixture separates into two layers: the top water layer and the dense, light-brownish bottom layer. The contents of the flask are poured into a porcelain dish and allowed to stand. The upper water layer is then decanted. The liquid resin which remains in the dish is washed with warm water until methyl orange shows a neutral reaction. It is then dried, gradually heating it to 200°C.

Novolak is used for obtaining moulding powders out of which technical and household articles are made.

Main reaction:



Reagents and Equipment

Phenol	8.4 g	Flask, round-bottom (100 ml) . . .	1
Formalin, 40 per cent . . .	9.4 g	Condenser, Liebig	1
	or 9 ml	Dish, porcelain	1
Ammonia, 25 per cent . . .	0.6 g	Thermometer	1
	or 0.6 ml		

Assembly

1. The 100-ml round-bottom flask is connected to a reflux condenser and placed in a water bath into which a thermometer is put.

Procedure

As much as 8.4 g of phenol, 9.4 g of 40 per cent formalin and 0.6 g of a 25 per cent ammonia solution are put in the 100-ml round-bottom flask. The mixture is then heated to 90°C in a water bath (apparatus 1). In 30-40 min, the reaction mixture will become turbid and separate into two layers: the top water layer and the bottom resinous layer. The mixture is then heated for another hour at 90°C. Afterwards, it is poured into a porcelain dish and cooled. The top water layer is decanted. The resinous layer is washed with water until the litmus shows a neutral reaction. It is then heated for 30 min at 60°C in a water bath. Resol, which is obtained as a sticky clear mass, is kept for another 4-6 h in an air bath at 75°C. A solid dense resin called resite is then obtained. The resite yield is about nine grams.

Resols are used for making textolite, moulding powders and anticorrosive lacquers.

Characterization Test. When resite is heated to 300°C in a test tube, it does not melt, but decomposes. The formaldehyde being evolved is determined by the fuchsin sulphurous acid test.

Chapter 20

IDENTIFICATION

Modern physicochemical methods of investigation, i.e., optical, spectral (ultraviolet, infrared and mass spectroscopy, nuclear magnetic resonance, etc.) and X-ray diffraction methods, make it possible to quickly determine the structure of organic compounds.

Apart from them, chemical methods for determining the structure of organic substances are also used. To identify a substance, it is first necessary to carry out preliminary tests so as to determine the class to which it belongs. The conclusions drawn are then confirmed by the appropriate qualitative tests for a given class.

To completely identify a test substance, it is necessary to obtain a solid crystalline derivative with a constant melting point, and then to determine this point. It is expedient to obtain a derivative with the highest melting point whenever possible.

Supplements 10-16 give the melting points of a series of derivatives of some compounds belonging to the most important classes.

To carry out identification operations, it is necessary to have a set of vessels for work with small amounts of a substance, i.e., a small Büchner funnel, a suction bottle (or test tube), a flask with a reflux condenser, and a distilling apparatus.

Many reactions can be carried out in test tubes. To carry out extraction, it is better to use a test tube and a pipette. Before filtering off the crystalline precipitate in the Büchner funnel, part of the precipitate can be pressed on filter paper. It can then be washed with a few drops of a solvent and its melting point can be determined.

It is expedient to identify substances which belong to the following classes: alcohols and phenols, aldehydes and ketones, carboxylic acids and their derivatives, amines and nitro compounds, and hydrocarbons and halides.

20.1. PRELIMINARY TESTS

Several conclusions are drawn from the odour and colour of a substance. Next, its physical constants are determined. Its melting point is determined in Thiele's apparatus, and its boiling point, in a simple distilling apparatus. When small quantities are involved,

it is better to use the micro method as follows: 5-10 drops of a test substance are put in a test tube, and then a capillary tube resealed 4-5 mm away from the lower open end is put into the liquid. The test tube is attached to a thermometer by a rubber band and heated in a bath (oil or glycerol). At first, bubbles come out of the capillary tube one at a time; when a stream of bubbles begins to come out, heating is stopped and the bath is allowed to cool.

The sought-for boiling point is the temperature at which the last bubble has left and the capillary begins to be filled with liquid.

When the boiling point has been determined, further preliminary tests are carried out.

Combustion Test. A few crystals or drops of a substance are put on a small metallic spoon and slowly burned in a burner flame. The observations made during combustion serve as a clue for preliminarily determining the class to which a substance belongs.

When unsaturated compounds (including aromatic ones) burn, they form a great deal of soot (smoky flame). When aliphatic hydrocarbons burn, they produce a bright flame and form a small amount of soot. Alcohols, i.e., oxygen-containing substances, burn with a slightly bright flame. If the residue on the spatula does not burn away, it can be assumed that metals are present. Substances which contain sulphur can be identified by the odour of sulphur dioxide.

Belstein Test. An ignited copper wire is put into a test substance and then into a colourless burner flame. If the flame turns green, it means that a halogen is present in the organic substance.

Test with Sulphuric Acid. Two millilitres of cold concentrated sulphuric acid with 1 ml of a test substance are vigorously shaken in a test tube. Saturated and aromatic hydrocarbons as well as their nitro and halogen derivatives do not dissolve. Unsaturated hydrocarbons, alcohols, ethers and esters usually dissolve without producing a colour. When aliphatic carbonyl compounds dissolve, they produce a dark hue.

Permanganate Test (according to Wagner). A test substance weighing 0.1-0.2 g is dissolved in 2 ml of water, alcohol or acetone. Afterwards, an aqueous 1-3 per cent potassium permanganate solution is added dropwise while stirring vigorously. If unsaturated hydrocarbons, aldehydes, formic acid, polyhydric phenols and aminophenols are present, the permanganate colour as a rule disappears and a precipitate of manganese dioxide is formed. The test should be regarded as positive if at least ten drops of the permanganate solution rapidly decolorize.

Test with Bromine. A 4 per cent solution of bromine in carbon tetrachloride is added dropwise to a solution of 0.1-0.2 g of a test substance in 2 ml of carbon tetrachloride (cool well). In the presence of unsaturated compounds, the brown colour of bromine disappears as a result of the addition reaction. A substitution reaction is occurring if decolorization is accompanied by the liberation of hydrogen bromide (bubbles). Under these conditions, phenols and aromatic amines are capable of replacing hydrogen by bromine.

Solubility Test. A test substance weighing 0.1-0.2 g is put into a test tube and 3 ml of a solvent are gradually added while vigorously shaking the test tube after every addition. Whenever necessary, the test tube is heated so as to completely dissolve the contents.

Since the test substance may undergo hydrolysis, especially when heated with acids or alkalies, it must, whenever possible, be isolated again after dissolution and identified by its melting or boiling point.

Solubility is tested in water, ethyl ether, 5 per cent alkali, a 5 per cent sodium bicarbonate solution, and in 5 per cent hydrochloric acid. Organic substances can be divided into four groups according to their solubility in water and ethyl ether.

Group I (soluble in ethyl ether and either insoluble or sparingly soluble in water): hydrocarbons, their halides, higher alcohols, most carbonyl compounds, amines, carboxylic acids and their derivatives, phenols, ethers and esters.

Group II (soluble in water and either insoluble or sparingly soluble in ethyl ether): acetone, methyl ethyl ketone, formaldehyde, acetaldehyde, propionaldehyde, formic, acetic and propionic acids, polyhydric alcohols, acid amides, salts, hydroxy acids, and di- and tricarboxylic acids.

Group III (soluble in both water and ethyl ether): low-molecular-weight carbonyl compounds, aliphatic hydroxy compounds, aliphatic nitriles, carboxylic acids, hydroxy acids, keto acids, polyhydric phenols, and amines.

Group IV (sparingly soluble in both water and ethyl ether): high-molecular-weight compounds, higher acid amides, and anthraquinones.

Such compounds as acid anhydrides and halides, which decompose by hydrolysis when water acts on them for more or less a long time, can be found as hydrolysates in one of the four groups.

All water-soluble substances (Groups II and III) and substances of a basic nature, i.e., primary, secondary and tertiary aliphatic amines, primary aromatic amines, and fatty aromatic amines containing not more than one aromatic residue, dissolve

in dilute hydrochloric acid. Some oxygen-containing compounds, e.g., ethyl ether, butyl alcohol and low-molecular-weight esters, dissolve in 5 per cent hydrochloric acid.

All strongly acidic substances, e.g., carboxylic acids, dissolve in a dilute sodium bicarbonate solution. Phenols, primary and secondary nitro compounds, and aryl sulphonyl derivatives of primary amines dissolve in dilute alkali.

20.2. QUALITATIVE REACTIONS

Acid Anhydrides and Halides. Three drops of the test substance are introduced into a reaction with five drops of aniline. If the test substance is a solid, 0.1 g of it is dissolved in 1 ml of hot benzene, and then aniline is added to the clear solution.

Acid anhydrides and halides react with aniline, evolving heat. The reaction products are solids called anilides. If crystals are not formed, crystallization can be produced by rubbing the side of the vessel with a rod.

Acids. Four drops of a substance (or 0.1 g) are dissolved in 2 ml of water or aqueous alcohol. The solution produces an acid reaction by litmus. The reaction continues even when a drop of a 10 per cent soda solution is added. Acid anhydrides and halides, as well as some esters, act similarly.

Amines. Water-soluble amines are identified by the alkaline reaction of their aqueous solution (four drops of a substance in 2 ml of water). The alkaline reaction (shown by litmus) continues even when a drop of glacial acetic acid is added.

Water-insoluble amines, whose carbon chain consists of 6-10 atoms, can be identified by their solubility in 5 per cent hydrochloric acid (four drops or 0.1 g of a substance in 2 ml of hydrochloric acid). Water-insoluble amines, whose chain consists of more than ten carbon atoms, are shaken with 5 per cent hydrochloric acid (0.1 g of a substance and 2 ml of hydrochloric acid) and then filtered off. An equal volume of a 10 per cent soda solution is added to the clear filtrate. Precipitation or great turbidity indicates the presence of amine.

After establishing the presence of amine, it is necessary to determine whether the amine is primary, secondary or tertiary. Only primary and secondary amines are capable of undergoing acylation reactions. This fact can be used for identifying them. The acetyl chloride test can be used for distinguishing a tertiary amine from a primary or secondary one.

A vigorous reaction occurs when acetyl chloride is added dropwise with a pipette to 0.5 ml of a primary or secondary amine. Scarcely any heat is evolved when acetyl chloride acts on tertiary amine.

Solid amines are dissolved in benzene before carrying out a reaction.

Phenols. A drop or 0.02 g of a test substance is dissolved in 1 ml of ethyl alcohol. Next, 1 ml of water and then a few drops of a 5 per cent ferric chloride solution are added. The presence of phenol is detected by the appearance of a green, violet or red colour.

Since ferric chloride is yellow, the appearance of a yellow or brown colour should be regarded as a negative result of the test. The test is negative when thymol, hydroquinone, 4-hydroxydiphenyl, *o*-nitrophenol and picric acid are involved. Some amines and sodium acetate produce a reddish colour.

Alcohols. A test substance measuring 0.5 ml is put into a dry test tube and the temperature is measured. Two drops of acetyl chloride are then added while stirring the contents with the thermometer. The occurrence of a vigorous reaction (heating) means that primary or secondary alcohol is present. If a reaction does not occur, five more drops of acetyl chloride are added and the temperature is watched. An elevation of temperature by more than 10°C means that tertiary alcohol is present.

If the test substance is a solid, 0.5 g of it is dissolved in 1 ml of warm benzene and the solution is cooled to 20°C and the temperature measured. Seven drops of acetyl chloride are then added while stirring the mixture. An elevation of temperature by more than 5°C means that alcohol is present.

Water, phenols and amines also produce this reaction.

Aldehydes. A drop of a test substance is added to 1 ml of fuchsin sulphurous acid. Aldehydes immediately produce an intense violet colour.

When water-insoluble substances are involved, two drops (or 0.05 g of a solid) are dissolved in 1 ml of alcohol, and then 1 ml of fuchsin sulphurous acid is added to the solution. The result is considered to be negative if a violet colour does not appear for 15 sec. The colour can be caused by atmospheric oxygen if the solution stands longer.

Esters. One millilitre of a 1 *N* potassium hydroxide solution in ethyl alcohol and three drops of an aqueous 40 per cent hydroxylamine hydrochloride solution are mixed in a test tube. The clear solution is decanted from the precipitate formed, and two drops (or 0.05 g) of a test substance are added to the solution. The mixture is heated to boiling for a minute. It is then cooled. Afterwards, a drop of a 5 per cent ferric chloride solution and ten drops of 2 *N* hydrochloric acid are added so as to dissolve the precipitate which can originate in some cases. The appearance of red or purple colour is considered to be a positive test for an ester.

Ketones. Semicarbazone or 2,4-dinitrophenylhydrazone can be obtained (see p. 326).

Nitriles and Amides. When they are heated with an aqueous potassium hydroxide solution, hydrolysis occurs with the evolution of ammonia or amine.

Five granules of potassium hydroxide are dissolved in five drops of water, and 2 ml of diethylene glycol and eight drops (or 0.2 g) of a test substance are added. The mixture is carefully heated until it boils, checking the vapour reaction with moist litmus paper. Red litmus test paper will turn blue if ammonia or aliphatic amine is formed. There may be an error in judgement if drops of the alkaline solution fall on the test paper.

A similar result is obtained when aliphatic amine salts are heated with alkali.

Nitro Compounds. Hydroxylamines, which are capable of isolating metallic silver from an ammonia solution of silver nitrate, are formed when nitro compounds are reduced in a neutral solution.

A test substance weighing 0.3 g is dissolved in 10 ml of 50 per cent alcohol. Afterwards, 0.5 g of ammonium chloride and 0.5 g of zinc dust are added. The mixture is then shaken and heated to boiling for two minutes. After cooling, it is filtered off and an ammonia solution of silver nitrate is added. The isolation of metallic silver (a grey flaky precipitate) means that the nitro or the nitroso group is present.

Halides. If a test substance does not dissolve in water and in concentrated hydrochloric and sulphuric acids, and if preliminary tests show that a halogen is present in the substance, it can be concluded that the substance is either an aromatic or a saturated aliphatic halide.

Hydrocarbons. A test substance is usually a hydrocarbon if tests show that it does not belong to any of the foregoing classes.

Saturated aliphatic hydrocarbons do not dissolve in water as well as concentrated sulphuric acid on heating. Unsaturated hydrocarbons (alkenes) dissolve in concentrated sulphuric acid and add bromine.

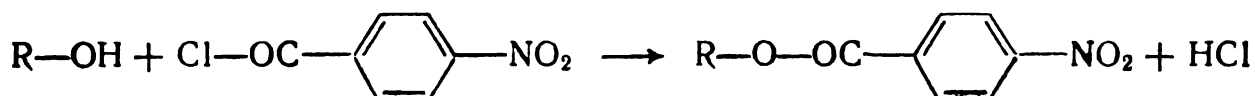
To determine a test substance, it is dissolved in carbon tetrachloride. Bromine, also dissolved in carbon tetrachloride, is then added to the solution. If instantaneous decolorization occurs, the presence of a double bond is very probable. Alkenes are not present in the test when decolorization occurs slowly when hydrogen-bromide turbidity appears.

In the cold, aromatic hydrocarbons do not dissolve in concentrated sulphuric acid, but they may dissolve on heating. Moreover, they undergo nitration.

20.3. PREPARATION OF DERIVATIVES

ALCOHOL DERIVATIVES

Esters of benzoic, p-nitrobenzoic or 3,5-dinitrobenzoic acids

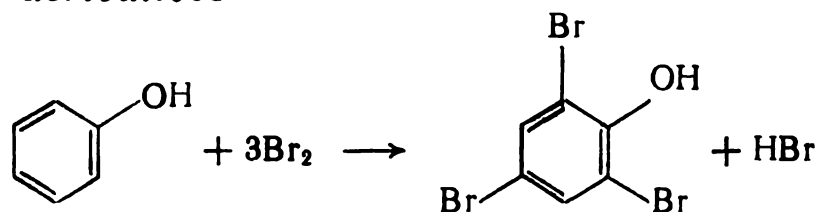


Twenty drops of benzoyl chloride or 0.5 g of *p*-nitro- or 3,5-dinitrobenzoyl chloride are added to 0.5 g (or twenty drops) of alcohol or phenol in a test tube. The solution is heated while being shaken, for 3-5 min in a boiling water bath, and then cooled and shaken together with 10 ml of a 5 per cent soda solution. The solid precipitate is filtered off, and then washed with water and recrystallized from dilute ethyl alcohol. If the alcohol is sensitive to the action of acids (tertiary alcohols), it is dissolved in 1 ml of pyridine, and then an acid chloride is added.

PHENOL DERIVATIVES

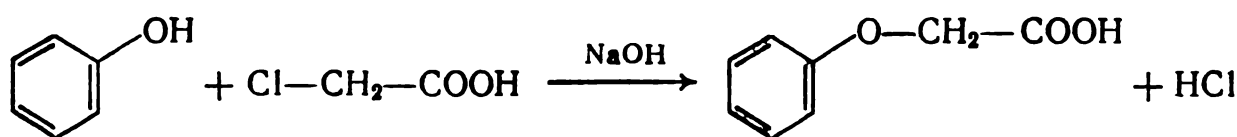
Esters of benzoic, p-nitrobenzoic and 3,5-dinitrobenzoic acids are obtained in the way described above for alcohols.

Bromine derivatives



A small amount of phenol is dissolved in water or acetone. Then a bromine solution (2 ml of bromine and 5 g of potassium bromide in 50 ml of water) is added dropwise, while shaking, until decolorization ceases. The precipitate obtained is sucked off and washed well with water. It is recrystallized from 96 or 50 per cent ethyl alcohol.

Phenoxyacetic acid

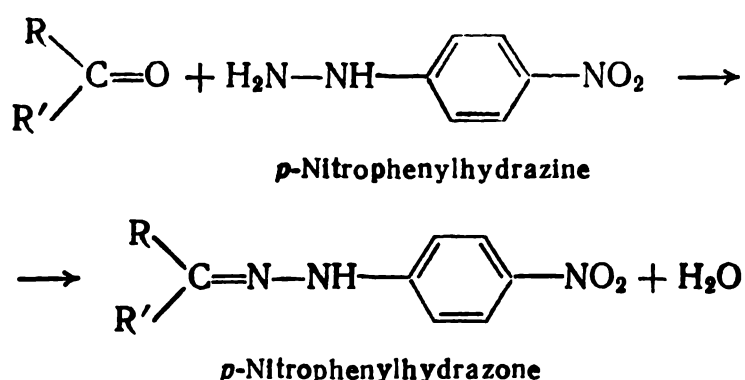


As much as 1.5-2 g of sodium hydroxide dissolved in 3 ml of water are added to a solution of 1 g of chloroacetic acid and 0.6 g of phenol in 2 ml of water. More water is added whenever necessary until dissolution is completed. The mixture is then heated at 80-100°C for 30-60 min. Afterwards, it is cooled and neutralized with dilute hydrochloric acid, using congo red or methyl orange to check neutralization. Phenoxyacetic acid is then ex-

tracted with ether. The ethereal layer is washed with water and shaken with a dilute soda solution. Phenoxyacetic acid passes as sodium salt into the soda solution, from which it is isolated by acidification with hydrochloric acid. Phenoxyacetic acid is sucked off and recrystallized from water.

ALDEHYDE AND KETONE DERIVATIVES

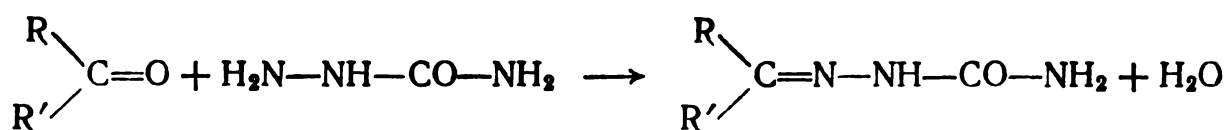
p-Nitrophenylhydrazones or 2,4-dinitrophenylhydrazones



A mixture of 0.7 g of *p*-nitrophenyl- or 2,4-dinitrophenylhydrazine and 1 g (or 1 ml) of a carbonyl compound together with 25 ml of alcohol is heated to boiling in a round-bottom flask fitted with a reflux condenser. A catalyst, i.e., 1 ml of concentrated hydrochloric acid, is added through the condenser.

The derivative should precipitate after the solution is allowed to boil for 15 min and then cooled. The precipitate is recrystallized from alcohol.

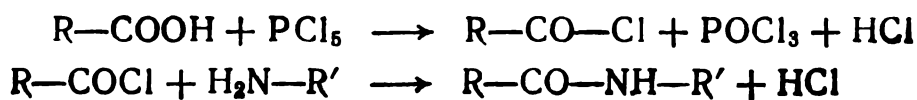
Semicarbazones



As much as 0.5 g of semicarbazide hydrochloride and 1 g of sodium acetate are dissolved in 3 ml of water in a test tube. Afterwards, 20 drops (or 0.5 g) of a carbonyl compound and enough alcohol for obtaining a homogeneous solution are added to the solution. The solution is heated for 10 min in a boiling water bath, and then cooled. The precipitate formed is filtered off and recrystallized from dilute alcohol.

CARBOXYLIC ACID DERIVATIVES

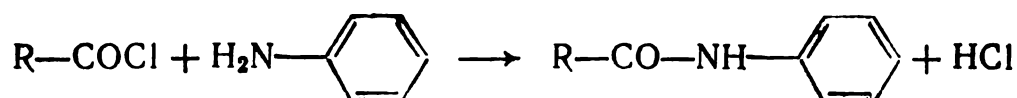
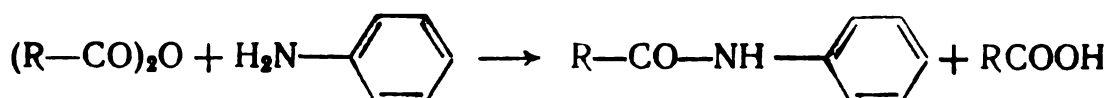
Anilides



A mixture of 0.2-0.3 g of anhydrous acid and a small excess of phosphorus pentachloride is heated for a few minutes in a hot water bath in a fume cupboard. The cooled reaction mixture is then dissolved in several millilitres of petroleum ether. To remove phosphorus oxychloride, the solution is shaken with a small amount (a few drops) of water. The acid chloride solution obtained is immediately used for further reaction.

To obtain anilide, about 20 drops of aniline are added, while shaking, to a solution of acid chloride in petroleum ether. After the reaction, the mixture is shaken with a few millilitres of a dilute sodium hydroxide solution. The reaction product is filtered off and washed once with a small amount of dilute hydrochloric acid and a dilute sodium bicarbonate solution. The product is recrystallized from a small amount of alcohol.

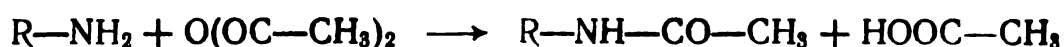
Acid anhydrides and chlorides



Twenty drops of aniline and 5 ml of a 10 per cent sodium hydroxide solution are carefully added to the test substance (20 drops or about 0.5 g). The mixture is stirred and heated for a minute in a boiling water bath, and then cooled. Anilide crystallizes out well if aniline is not in excess. If crystallization does not occur, the oil obtained is separated and washed with dilute hydrochloric acid. The crystals obtained are recrystallized from ethyl alcohol or a mixture of it and water.

PRIMARY AND SECONDARY AMINE DERIVATIVES

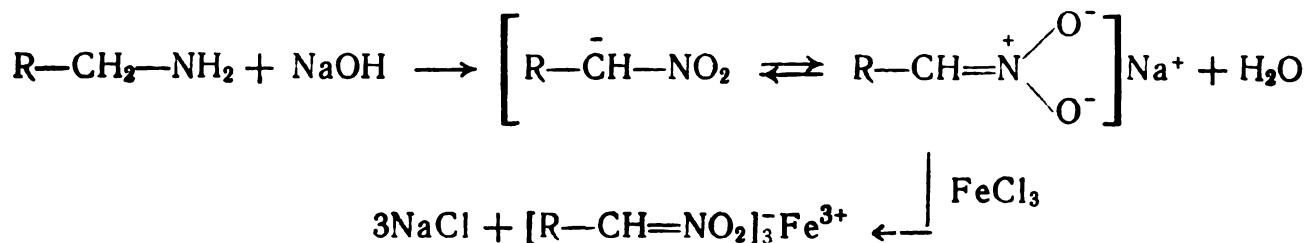
Acetamides (from amines containing more than five carbon atoms)



Twenty drops (or 0.5 g) of amine are mixed with 20 drops of acetic anhydride in a test tube, and the mixture is heated for a few minutes at 80-90 °C in a water bath. When cooled, the mixture is added to a small amount of water. The reaction product begins to crystallize when the side of the vessel is rubbed with a glass rod. The crystals are washed with water and recrystallized from alcohol, a water-alcohol mixture or cyclohexane.

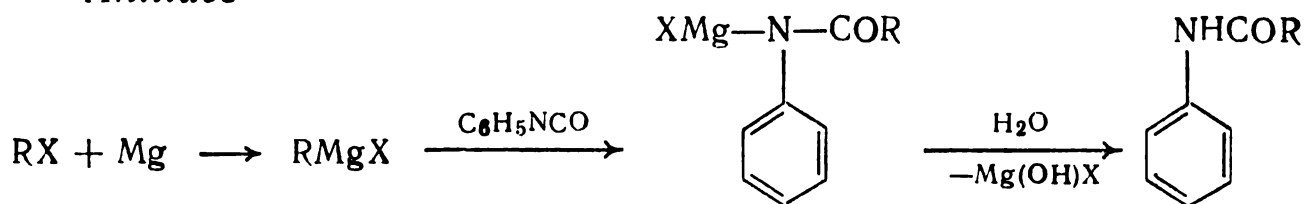
NITRO DERIVATIVES

A colour reaction involving ferric chloride and alkali is carried out (for primary and secondary aliphatic nitro compounds):



The nitro compound is converted into a sodium salt of the *aci* form by treating it with a small amount of a concentrated sodium hydroxide solution. The solution of this salt in water produces a blood-red colour when 3 per cent ferric chloride is added.

ALKYL HALIDE DERIVATIVES

Anilides

Magnesium chips (0.3-0.5 g) are activated by heating them with an iodine crystal. Then, 5-10 ml of absolute ethyl ether and 1 ml of the halide are added. When the reaction begins, the mixture is so heated for 20 min in a water bath that the ether boils slightly.*

When almost all the magnesium has dissolved, the solution is filtered off and 0.5 ml of phenylisocyanate in a small amount of ether is added to the filtrate. Somewhat later, the cooled solution is poured into a few millilitres of cold water, to which about 1 ml of concentrated hydrochloric acid has been added beforehand. The ethereal layer is separated and dried with sodium sulphate, and then ether is driven off. The residue is crystallized from ethyl alcohol.

RECOMMENDED LITERATURE

Voskresensky, T. I., *Techniques of Laboratory Operations*. Tenth edition, Khimiya, Moscow, 1973 (in Russian).

Potapov, V. M. and Tatarinchik, S. N., *Organic Chemistry*. Mir Publishers, Moscow, 1979.

Preparative Organic Chemistry. Second edition, Khimiya, Moscow, 1964 (in Russian).

* The reaction must be carried out in a flask fitted with a reflux condenser and a calcium chloride tube.

SUPPLEMENTS

Supplement 1

Drying Agents for Organic Compounds

Organic compounds	Drying agents
Hydrocarbons	CaCl ₂ , CaSO ₄ , P ₂ O ₅ , Na
Halides	CaCl ₂ , Na ₂ SO ₄ , MgSO ₄ , P ₂ O ₅
Alcohols	MgSO ₄ , CaSO ₄ , K ₂ CO ₃ , CaO
Ethers	CaCl ₂ , CaSO ₄ , Na
Aldehydes	CaCl ₂ , MgSO ₄ , Na ₂ SO ₄
Ketones	MgSO ₄ , Na ₂ SO ₄ , K ₂ CO ₃
Organic acids	MgSO ₄ , Na ₂ SO ₄ , CaSO ₄
Amines	KOH, NaOH, K ₂ CO ₃ , CaO
Nitro compounds	CaCl ₂ , Na ₂ SO ₄
Phenols	Na ₂ SO ₄

Supplement 2

Steam Pressure at Different Temperatures

Tempera- ture, °C	Pressure, mm Hg	Tempera- ture, °C	Pressure, mm Hg	Tempera- ture, °C	Pressure, mm Hg	Tempera- ture, °C	Pressure, mm Hg
60	149.3	70	233.7	80	355.1	90	525.8
61	156.4	71	243.9	81	369.7	91	546.0
62	163.8	72	254.6	82	384.9	92	567.0
63	171.4	73	265.7	83	400.6	93	588.6
64	179.3	74	277.2	84	416.8	94	610.9
65	187.5	75	289.1	85	433.3	95	633.9
66	196.1	76	301.4	86	450.9	96	657.6
67	205.0	77	314.1	87	468.7	97	682.1
68	214.2	78	327.3	88	487.1	98	707.3
69	223.7	79	341.0	89	506.1	99	733.2

Supplement 3

Pressure of Liquefied Gases in Cylinders

Gas	Bolling point, °C	Critical point, °C	Overpressure at 20 °C, kg/cm ²
Carbon dioxide	−78.2	+31.1	55.25
Ammonia	−33.4	+132.4	7.46
Hydrogen sulphide	−60	+100.4	16.7
Chlorine	−83.6	+144.0	5.62

Supplement 4

Colour Code of Compressed Gas Cylinders

Gas	Cylinder colour	Inscription colour
Nitrogen	Black	Yellow
Ammonia	Dark yellow	Black
Acetylene	White	Red
Hydrogen	Dark green	Red
Oxygen	Light blue	Black
Sulphur dioxide	Black	White
Carbon dioxide	Black	Yellow

Supplement 5

Density of Sulphuric Acid Solutions (20 °C)

<i>d</i>	%	mole/l	g/l	<i>d</i>	%	mole/l	g/l
1.000	0.261	0.0266	2.608	1.095	14.04	1.567	153.7
005	0.986	0.1010	9.906	100	14.73	1.652	162.0
010	1.731	0.1783	17.49	105	15.41	1.735	170.2
015	2.485	0.2595	25.45	110	16.08	1.820	178.5
020	3.242	0.3372	33.07	115	16.76	1.905	186.8
025	4.000	0.4180	41.99	120	17.43	1.990	195.2
030	4.746	0.4983	48.87	125	18.09	2.075	203.5
035	5.493	0.5796	56.85	130	18.76	2.161	211.9
040	6.237	0.6613	64.86	135	19.42	2.247	220.4
045	6.956	0.7411	72.69	170	23.95	2.857	280.2
050	7.704	0.8250	80.92	175	24.58	2.945	288.8
055	8.415	0.9054	88.80	180	25.21	3.033	297.5
060	9.129	0.9856	96.67	185	25.84	3.122	306.2
065	9.843	1.066	104.6	190	26.47	3.211	314.9
070	10.56	1.152	113.0	195	27.10	3.302	323.9
075	11.26	1.235	121.1	200	27.72	3.391	332.6
080	11.96	1.317	129.2	205	28.33	3.481	341.4
085	12.66	1.401	137.4	210	28.95	3.572	350.3
090	13.36	1.484	145.6	215	29.57	3.663	359.3

Supplement 5, continued

<i>d</i>	%	mole/l	g/l	<i>d</i>	%	mole/l	g/l
1.220	30.18	3.754	368.2	1.490	59.24	9.000	882.7
225	30.79	3.846	377.2	495	59.70	9.100	892.5
230	31.40	3.938	386.2	500	60.17	9.202	902.5
235	32.01	4.031	395.4	505	60.62	9.303	912.4
240	32.61	4.123	404.4	510	61.08	9.404	922.3
245	33.22	4.216	413.5	515	61.54	9.506	932.3
250	33.82	4.310	422.7	520	62.00	9.608	942.4
255	34.42	4.404	431.9	525	62.45	9.711	952.5
260	35.01	4.498	441.2	530	62.91	9.813	962.5
265	35.60	4.592	450.4	535	63.36	9.916	972.6
270	36.19	4.686	459.6	540	63.81	10.02	982.8
275	36.78	4.781	468.9	545	64.26	10.12	992.6
280	37.36	4.876	478.2	550	64.71	10.23	1003
285	37.95	4.972	487.6	555	65.15	10.33	1013
290	38.53	5.068	497.1	560	65.59	10.43	1023
295	39.10	5.163	506.4	565	66.03	10.54	1034
300	39.68	5.259	515.8	570	66.47	10.64	1044
305	40.25	5.356	525.3	575	66.91	10.74	1053
310	40.82	5.452	534.7	580	67.35	10.85	1064
315	41.39	5.549	544.2	585	67.79	10.96	1075
320	41.95	5.646	553.8	590	68.23	11.06	1085
325	42.51	5.743	563.3	595	68.66	11.16	1095
330	43.07	5.840	572.8	600	69.09	11.27	1105
335	43.62	5.938	582.4	605	69.53	11.38	1116
340	44.17	6.035	591.9	610	69.96	11.48	1126
345	44.72	6.132	601.4	615	70.39	11.59	1136
350	45.26	6.229	610.9	620	70.82	11.70	1148
355	45.80	6.327	620.6	625	71.25	11.80	1157
360	46.33	6.424	630.1	630	71.76	11.91	1168
365	46.86	6.522	639.7	635	72.09	12.02	1179
370	47.39	6.620	649.3	640	72.52	12.13	1190
375	47.92	6.718	658.9	645	72.95	12.24	1200
380	48.45	6.817	668.6	650	73.37	12.34	1210
385	48.97	6.915	678.2	655	73.80	12.45	1221
390	49.48	7.012	687.7	660	74.22	12.56	1232
395	49.99	7.110	697.3	665	74.64	12.67	1243
400	50.50	7.208	707.0	670	75.07	12.78	1253
405	51.01	7.307	716.7	675	75.49	12.89	1264
410	51.52	7.406	726.4	680	75.92	13.00	1275
415	52.02	7.505	736.1	685	76.34	13.12	1287
420	52.51	7.603	745.7	690	76.77	13.23	1298
425	53.01	7.702	755.4	695	77.20	13.34	1308
430	53.50	7.801	765.1	700	77.63	13.46	1320
435	54.00	7.901	774.9	705	78.06	13.57	1331
440	54.49	8.000	784.6	710	78.49	13.69	1343
445	54.97	8.099	794.3	715	78.93	13.80	1354
450	55.45	8.198	804.1	720	79.37	13.92	1365
455	55.93	8.297	813.8	725	79.81	14.04	1377
460	56.41	8.397	823.6	730	80.25	14.16	1389
465	56.89	8.497	833.4	735	80.70	14.28	1401
470	57.36	8.598	843.3	740	81.16	14.40	1412
475	57.84	8.699	853.2	745	81.62	14.52	1424
480	58.31	8.799	863.0	750	82.09	14.65	1437
485	58.78	8.899	872.8	755	82.57	14.78	1450

Supplement 5, concluded

<i>d</i>	%	mole/l	g/l	<i>d</i>	%	mole/l	g/l
1.760	83.06	14.90	1461	1.822	91.56	17.01	1668
765	83.57	14.98	1469	823	91.78	17.06	1673
770	84.08	15.17	1488	824	92.00	17.11	1678
775	84.61	15.31	1502	825	92.25	17.17	1684
780	85.16	15.46	1516	826	92.51	17.22	1689
785	85.74	15.61	1531	827	92.77	17.28	1695
790	86.35	15.76	1546	828	93.03	17.34	1701
795	86.99	15.92	1561	829	93.33	17.40	1707
800	87.69	16.09	1578	830	93.64	17.47	1713
805	88.43	16.27	1596	831	93.94	17.54	1720
810	89.23	16.47	1615	832	94.32	17.62	1728
815	90.12	16.68	1636	833	94.72	17.70	1736
820	91.11	16.91	1659	834	95.12	17.79	1745
821	91.33	16.96	1663	835	95.72	17.91	1757

Supplement 6

Density of Hydrochloric Acid Solutions (20 °C)

<i>d</i>	%	mole/l	g/l	<i>d</i>	%	mole/l	g/l
1.000	0.360	0.0987	3.599	1.095	19.41	5.829	212.5
005	1.360	0.3745	13.65	100	20.39	6.150	224.2
010	2.364	0.6547	23.87	105	21.36	6.472	236.0
015	3.374	0.939	34.24	110	22.33	6.796	247.8
020	4.388	1.227	44.74	115	23.29	7.122	259.7
025	5.408	1.520	55.42	120	24.25	7.449	271.6
030	6.433	1.817	66.25	125	25.22	7.782	283.7
035	7.464	2.118	77.22	130	26.20	8.118	396.0
040	8.490	2.421	88.27	135	27.18	8.459	308.4
045	9.510	2.725	99.35	140	28.18	8.809	321.2
050	10.52	3.029	110.4	145	29.17	9.159	333.9
055	11.52	3.333	121.5	150	30.14	9.505	346.6
060	12.51	3.638	132.6	155	31.14	9.863	359.6
065	13.50	3.944	143.8	160	32.14	10.22 ₅	372.8
070	14.49 ₅	4.253	155.1	165	33.16	10.59 ₅	386.3
075	15.48 ₅	4.565	166.4	170	34.18	10.97	399.9
080	16.47	4.878	177.8	180	36.23	11.73	427.7
085	17.45	5.192	189.3	190	38.32	12.50	455.8
090	18.43	5.509 ₅	200.9	198	40.00	13.14	479.1

Supplement 7

Density of Nitric Acid Solutions (20 °C)

<i>d</i>	%	mole/l	g/l	<i>d</i>	%	mole/l	g/l
1.000	0.3296	0.0523	3.295	015	3.073	0.4950	31.19
005	1.255	0.2001	12.61	020	3.982	0.6445	40.61
010	2.164	0.3468	21.85	025	4.883	0.7943	50.05

Supplement 7, concluded

<i>d</i>	%	mole/l	g/l	<i>d</i>	%	mole/l	g/l
1.030	5.784	0.9454	59.57	1.305	49.21	10.19	642.1
035	6.661	1.094	68.93	310	50.00	10.39	654.7
040	7.530	1.243	78.32	315	50.85	10.61	668.5
045	8.398	1.393	87.77	320	51.71	10.83	682.4
050	9.259	1.543	97.22	325	52.56	11.05	696.3
055	10.12	1.694	106.7	330	53.41	11.27	710.1
060	10.97	1.845	116.3	335	54.27	11.49	724.0
065	11.81	1.997	125.8	340	55.13	11.72	738.5
070	12.65	2.148	135.3	345	56.04	11.96	753.6
075	13.48	2.301	145.0	350	56.95	12.20	768.7
080	14.31	2.453	154.6	355	57.87	12.44	783.8
085	15.13	2.605	164.1	360	58.78	12.68	799.0
090	15.95	2.759	173.8	365	59.69	12.93	814.7
095	16.76	2.913	183.5	370	60.67	13.19	831.1
100	17.58	3.068	193.3	375	61.69	13.46	848.1
105	18.39	3.224	203.1	380	62.78	13.73	865.1
110	19.19	3.341	213.0	385	63.72	14.01	882.8
115	20.00	3.559	223.0	390	64.74	14.29	900.4
120	20.79	3.666	232.9	395	65.84	14.57	918.1
125	21.59	3.854	242.8	400	66.97	14.88	937.6
130	22.38	4.012	252.8	405	68.10	15.18	956.5
135	23.16	4.171	262.8	410	69.23	15.49	976.0
140	23.94	4.330	272.8	415	70.34	15.81	996.2
145	24.71	4.489	282.9	420	71.63	16.14	1017
150	25.48	4.649	292.0	425	72.86	16.47	1038
155	26.24	4.810	303.1	430	74.09	16.81	1059
160	27.00	4.970	313.2	435	75.35	17.16	1081
165	27.76	5.132	323.4	440	76.71	17.53	1105
170	28.51	5.293	333.5	445	78.07	17.90	1128
175	29.25	5.455	343.7	450	79.43	18.28	1152
180	30.00	5.618	354.0	455	80.88	18.68	1177
185	30.74	5.780	364.2	460	82.39	19.09	1203
190	31.47	5.943	374.5	465	83.91	19.51	1229
195	32.21	6.110	385.0	470	85.50	19.95	1257
200	32.94	6.273	395.3	475	87.29	20.43	1287
205	33.68	6.440	405.8	480	89.07	20.92	1318
210	34.41	6.607	416.3	485	91.13	21.48	1353
215	35.16	6.778	427.1	490	93.49	22.11	1393
220	35.93	6.956	438.3	495	95.46	22.65	1427
225	36.70	7.135	449.6	500	96.73	23.02	1450
230	37.48	7.315	460.9	501	96.98	23.10	1456
235	38.25	7.497	472.4	502	97.23	23.18	1461
240	39.02	7.679	483.8	503	97.49	23.25	1465
250	40.58	8.049	507.2	504	97.74	23.33	1470
255	41.36	8.237	519.0	505	97.99	23.40	1474
260	42.14	8.426	530.9	506	98.25	23.48	1479
265	42.92	8.616	542.9	507	98.50	23.56	1485
270	43.70	8.808	555.0	508	98.76	23.63	1488
275	44.48	9.001	567.2	509	99.01	23.71	1494
280	45.27	9.195	579.4	510	99.26	23.79	1499
285	46.06	9.394	591.9	511	99.52	23.86	1503
290	46.85	9.590	604.3	512	99.77	23.94	1508
295	47.63	9.789	616.8	513	100.00	24.01	1513
300	48.42	9.990	629.5				

Supplement 8
Density of Sodium Hydroxide Solutions (20 °C)

<i>d</i>	%	mole/l	g/l		<i>d</i>	%	mole/l	g/l
1.000	0.159	0.0398	1.592		1.270	24.64	7.824	313.0
005	0.602	0.151	6.040		275	25.10	8.000	320.0
010	1.04	0.264	10.56		280	25.56	8.178	327.1
015	1.49	0.378	15.12		285	26.02	8.387	334.3
020	1.94	0.494	19.76		290	26.48	8.539	341.6
025	2.39	0.611	24.44		295	26.94	8.722	348.9
030	2.84	0.731	29.24		300	27.41	8.906	356.2
035	3.29	0.851	34.04		305	27.87	9.092	363.7
040	3.74	0.971	38.84		310	28.33	9.278	371.2
045	4.20	1.097	43.88		315	28.80	9.466	378.6
050	4.65	1.222	48.88		320	29.26	9.656	386.2
055	5.11	1.347	53.88		325	29.73	9.847	393.9
060	5.56	1.474	58.96		330	30.20	10.04	401.6
065	6.02	1.602	64.08		335	30.67	10.23	409.2
070	6.47	1.731	69.24		340	31.14	10.43	417.2
075	6.93	1.862	74.48		345	31.62	10.63	425.2
080	7.38	1.992	79.68		350	32.10	10.83	433.2
085	7.83	2.123	84.92		355	32.58	11.03	441.2
090	8.28	2.257	90.28		360	33.06	11.24	449.6
095	8.74	2.391	95.64		365	33.54	11.45	458.0
100	9.19	2.527	101.1		370	34.03	11.65	466.7
105	9.64	2.664	106.6		375	34.52	11.86	474.4
110	10.10	2.802	112.1		380	35.01	12.08	483.2
115	10.55	2.942	117.7		385	35.50	12.29	491.6
120	11.01	3.082	123.3		390	36.00	12.51	500.4
125	11.46	3.224	129.0		395	36.49	12.73	509.2
130	11.92	3.367	134.7		400	36.99	12.95	518.0
135	12.37	3.510	140.4		405	37.49	13.17	526.8
140	12.83	3.655	146.2		410	37.99	13.39	535.6
145	13.28	3.801	152.0		415	38.49	13.61	544.4
150	13.73	3.947	157.9		420	38.99	13.84	553.6
155	14.18	4.095	163.8		425	39.40	14.07	562.8
160	14.64	4.244	169.8		430	40.00	14.39	572.0
165	15.09	4.395	175.8		435	40.51	14.53	581.2
170	15.54	4.545	181.8		440	41.03	14.77	590.8
175	15.99	4.697	187.9		445	41.55	15.01	600.4
180	16.44	4.850	194.0		450	42.07	15.25	610.0
185	16.89	5.004	200.2		455	42.59	15.49	619.6
190	17.34	5.160	206.4		460	43.12	15.74	629.6
195	17.80	5.317	212.7		465	43.64	15.98	639.2
200	18.25	5.476	219.0		470	44.17	16.23	649.2
205	18.71	5.636	225.4		475	44.69	16.48	659.2
210	19.16	5.796	231.8		480	45.22	16.73	669.2
215	19.62	5.958	238.3		485	45.75	16.98	679.2
220	20.07	6.122	244.9		490	46.27	17.23	689.2
225	20.53	6.286	251.4		495	46.80	17.49	699.6
230	20.98	6.451	258.0		500	47.33	17.75	710.0
235	21.44	6.619	264.8		505	47.85	18.00	720.0
240	21.90	6.788	271.5		510	48.38	18.26	730.4
245	22.36	6.958	278.3		515	48.90	18.52	740.8
250	22.82	7.129	285.2		520	49.44	18.78	751.2
255	23.27	7.302	292.1		525	49.97	19.05	762.0
260	23.73	7.475	299.0		530	50.50	19.31	772.4
265	24.19	7.650	306.0					

Supplement 9

Density of Potassium Hydroxide Solutions (20 °C)

<i>d</i>	%	mole/lit	g/lit	<i>d</i>	%	mole/lit	g/lit
1.000	0.197	0.035	1.964	1.270	28.29	6.40	359.1
005	0.743	0.133	7.463	275	28.77	6.54	367.0
010	1.295	0.233	13.07	280	29.25	6.67	374.3
015	1.84	0.333	18.68	285	29.73	6.81	382.1
020	2.38	0.433	24.30	290	30.21	6.95	390.0
025	2.93	0.536	30.07	295	30.68	7.08	397.3
030	3.48	0.639	35.85	300	31.15	7.22	405.1
035	4.03	0.744	41.75	305	31.62	7.36	413.0
040	4.58	0.848	47.58	310	32.09	7.49	420.3
045	5.12	0.954	53.53	315	32.56	7.63	428.1
050	5.66	1.06	59.48	320	33.03	7.77	436.0
055	6.20	1.17	65.65	325	33.50	7.91	443.8
060	6.74	1.27	71.26	330	33.97	8.05	451.7
065	7.28	1.38	77.43	335	34.43	8.19	459.5
070	7.82	1.49	83.60	340	34.90	8.33	467.7
075	8.36	1.60	89.78	345	35.36	8.48	475.8
080	8.89	1.71	95.95	350	35.82	8.62	483.7
085	8.96	1.82	102.1	355	36.28	8.76	491.4
090	9.43	1.94	108.9	360	36.73	8.90	499.4
095	10.49	2.05	115.0	365	37.19	9.05	507.8
100	11.03	2.16	121.2	370	37.65	9.19	515.7
105	11.56	2.28	127.9	375	38.10	9.34	524.1
110	12.08	2.39	134.1	380	38.56	9.48	531.9
115	12.61	2.51	140.8	385	39.01	9.63	540.3
120	13.14	2.62	147.0	390	39.49	9.78	548.8
125	13.66	2.74	153.7	395	39.92	9.93	557.2
130	14.19	2.86	160.5	400	40.37	10.07	565.0
135	14.70	2.97	166.6	405	40.82	10.22	573.4
140	15.22	3.09	173.4	410	41.26	10.37	581.9
145	15.74	3.21	180.1	415	41.71	10.52	590.3
150	16.26	3.33	186.6	420	42.15	10.67	598.7
155	16.78	3.45	193.6	425	42.60	10.82	607.1
160	17.29	3.58	200.9	430	43.04	10.97	615.5
165	17.81	3.70	207.6	435	43.48	11.12	623.9
170	18.32	3.82	214.3	440	43.92	11.28	632.9
175	18.84	3.94	221.1	445	44.36	11.42	640.8
180	19.35	4.07	228.4	450	44.79	11.58	649.7
185	19.86	4.19	235.1	455	45.23	11.73	658.2
190	20.37	4.32	242.4	460	45.66	11.88	666.6
195	20.88	4.45	249.7	465	46.09	12.04	675.6
200	21.38	4.57	256.4	470	46.53	12.19	684.0
205	21.88	4.70	263.7	475	46.96	12.35	693.0
210	22.38	4.83	271.0	480	47.39	12.50	701.4
215	22.88	4.95	277.7	485	47.82	12.66	710.4
220	23.38	5.08	285.0	490	48.25	12.82	719.3
225	23.87	5.21	292.3	495	48.67	12.97	727.7
230	24.37	5.34	299.6	500	49.10	13.13	736.7
235	24.86	5.47	306.9	505	49.53	13.29	745.7
240	25.36	5.60	314.2	510	49.95	13.45	754.7
245	25.85	5.74	322.1	515	50.38	13.60	763.1
250	26.34	5.87	329.4	520	50.80	13.76	772.1
255	26.83	6.00	336.7	525	51.22	13.92	781.1
260	27.32	6.13	344.0	530	51.74	14.08	790.0
265	27.80	6.27	351.8	535	52.05	14.24	799.0

Supplement 10

Physical Properties of Alcohols and Their Derivatives

Alcohol	Temperature, °C	Melting point, °C	
		<i>p</i> -nitrobenzoate	3,5-dinitrobenzoate
Methyl	65	96 (180 mm) *	108
Ethyl	78	57	93
Isopropyl	82	110	123
<i>tert</i> -Butyl	83	116	143
Propyl	97	35	74
Allyl	97	29	50
<i>sec</i> -Butyl	99	26	76
<i>tert</i> -Amyl	102	85	117
Isobutyl	108	69	88
3-Pentanol	116	17	98
Butyl	118	36 (70 mm)	64
<i>sec</i> -Amyl	120	17	62
Amyl	138	11	46
Hexyl	157	5	61
Cyclohexanol	161	50	113
Ethylene glycol	198	141	169
Benzyl	205	86	113
1,4-Butanediol	230	175	—
Glycerol	290	188	—

* The pressure given in parentheses from here on is in mm Hg.

Supplement 11

Physical Properties of Phenols and Their Derivatives

Compound	Melting point, °C	Boiling point, °C	Melting point, °C				
			benzoate	bromine derivative	aryl hydroxyacetic acids	<i>p</i> -nitrobenzoate	3,5-dinitrobenzoate
Ethyl salicylate	1	234	87	—	—	108	—
<i>o</i> -Bromophenol . .	5	195	86	Tri- : 95	143	—	—
<i>o</i> -Chlorophenol . .	7	176	—	Di- : 76	—	115	143
<i>m</i> -Cresol	12	203	54	Tri- : 84	102	90	—
<i>o</i> -Cresol	31	192	—	Di- : 56	52	94	138
<i>m</i> -Bromophenol . .	32	236	86	—	108	—	—
Quaiacol	32	205	—	Tri- : 116	—	93	141
<i>m</i> -Chlorophenol . .	33	214	—	—	—	99	156
<i>p</i> -Cresol	36	202	—	Tetra- : 108	—	98	187
Phenol	42	183	68	Tri- : 95	99	127	146
<i>p</i> -Chlorophenol . .	43 (37 mm)	217	93	Di- : 90	156	171	186
<i>o</i> -Nitrophenol . . .	45	216	59	Di- : 117	—	141	155
<i>p</i> -Bromophenol . .	64	236	102	Di- : 95	157	180	191
α -Naphthol	94	280	56	Di- : 105	192	143	217
<i>m</i> -Nitrophenol . . .	97	194 (70 mm)	95	Di- : 91	—	174	159
Pyrocatechin . . .	105	246	Di- : 81	Tetra- : 192	—	169	152
Resorcin	110	280	Di- : 117	Di- : 116	195	182	201
<i>p</i> -Nitrophenol . . .	114	—	142	118 (142 mm)	—	159	188
β -Naphthol	123	286	107	84	155	169	210
Pyrogallol	133	301	Tri- : 90	Di- : 158	—	230	205
Hydroquinone . . .	169	286	Di- : 199	Di- : 186	—	258	317
Phloroglucinol . .	219	—	Tri- : 173	Tri- : 151	—	283	162

Supplement 12
Physical Properties of Aldehydes and Their Derivatives

Aldehyde	Boiling point, °C	Melting point, °C		
		<i>p</i> -nitrophe- nylhydra- zone	2,4-dinitro- phenylhydra- zone	semicarba- zone
Formaldehyde	−21	182	167	169
Acetaldehyde	21	129	168 (147 mm)	162
Propionaldehyde	49	124	155	89 (154 mm)
Isobutyraldehyde	64	132	182	125
Butyraldehyde	74	92	122	106
Valeraldehyde	103	—	98 (107 mm)	—
Caproaldehyde	128	—	104	106
Furfural	161	54	214 (230 mm)	202
Succinaldehyde	170	—	280	—
Benzaldehyde	179	192	237	222
Salicylaldehyde	196	223	248	231

Supplement 13
Physical Properties of Ketones and Their Derivatives

Ketone	Boiling point, °C	Melting point, °C		
		<i>p</i> -nitrophenyl- hydrazone	2,4-dinitro- phenylhydra- zone	semicarba- zone
Acetone	56	150	128	189
Methyl ethyl ketone	80	129	117	146
Methyl isopropyl ketone	94	109	120	114
Diethyl ketone	102	144	156	139
Diisopropyl ketone	124	—	96	160

Supplement 14
Physical Properties of Carboxylic Acids and Their Derivatives

Acid	Melting point, °C	Boiling point, °C	Melting point of anilide, °C	Boiling point, °C	
				acid chloride	anhydride
Formic	8	100	50	—	—
Acetic	17	118	113	52	138
Acrylic	13	140	105	76	—
Propionic	—	140	105	80	168
Isobutyric	—	155	105	92	82
Butyric	—	163	96	100	98
Valeric	—	186	63	—	—
Dichloroacetic	—	194	119	107	215
Caproic	—	205	95	—	—
Oleic	14	223 (10 mm)	41	—	—
Citric	100	—	53 (199 mm)	—	—
Oxalic	101	—	90 (149 mm)	64	—
Adipic	153	—	161	148 (9 mm)	—
Salicylic	158	—	175	—	—
Phthalic	200	—	226	190	250

Supplement 15

Physical Properties of Primary and Secondary Amines and Their Derivatives (Acetamides)

Amine	Melting point, °C	Boiling point, °C	Melting point of acetamide, °C	Amine	Melting point, °C	Boiling point, °C	Melting point of acetamide, °C
Methylamine . . .	—	—6	28	<i>o</i> -Toluidine . .	—	200	111
Dimethylamine .	—	7	—	<i>m</i> -Toluidine . .	—	203	65
Ethylamine . . .	—	17	—	<i>m</i> -Bromaniline .	18	251	87
Diethylamine . .	—	56	—	<i>o</i> -Bromaniline .	32	229	99
Butylamine . . .	—	77	—	<i>p</i> -Toluidine . .	45	200	147
Isoamylamine . .	—	96	—	α -Naphthylamine	50	300	159
Amylamine . . .	—	104	—	Diphenylamine .	54	302	101
Benzylamine . .	—	184	65	<i>p</i> -Bromaniline .	66	245	168
Aniline	—	184	114	<i>o</i> -Nitroaniline .	71	—	93

Supplement 16

Physical Properties of Alkyl Halides and Their Derivatives (Anilides)

Alkyl halide	Melting point of anilide, °C	Alkyl halide	Melting point of anilide, °C
Methyl-	114	<i>tert</i> -Butyl-	128
Ethyl-	104	Isobutyl-	109
Isopropyl-	103	Butyl-	63
Propyl-	92	Isoamyl-	108
Allyl-	114	Amyl-	96

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G. Vinogradov, D. Sc. and A. Malkin, D. Sc.

This monograph presents a comprehensive, generalized treatment of theoretical and experimental investigations in the field of the rheology of high-molecular-mass compounds and their solutions, the properties of which are examined in relationship to their structure and composition.

The book describes all the most important manifestations of the specific features of the mechanical properties of polymers in the viscoelastic state, which forms the basis for a theoretically substantiated design calculation and selection of the processing equipment used for the moulding of various articles from polymeric materials. Much space is devoted to a detailed consideration of results of investigations of the viscous properties of polymer melts and solutions, which govern their behaviour in the various manufacturing processes.

The behaviour of fluid polymers under the conditions of uniaxial extension is treated in detail.

The book is intended for a wide circle of readers who are in any way concerned with the problems of physics, mechanics and physical chemistry of polymers and also for technologists engaged in plastics processing, moulding of articles from rubber mixes and production of fibres. The book will also be of assistance and guidance to students and post-graduates specializing in polymer science and technology.

THEORETICAL FOUNDATIONS OF MODERN CHEMICAL ANALYSIS

Yu. Lyalikov, D. Sc. and Yu. Klyachko, D. Sc.

This monograph deals with the basic principles of the unified modern theory of chemical qualitative analysis of inorganic substances. Offers analytical classifications of ions according to

their solubility, ability to form colour substances, extractability, chromatographic and electrochemical characteristics, etc.

Describes methods of concentrating, masking and separating the ions and molecules being determined. A separate chapter is devoted to methods of qualitative analysis of natural and industrial materials.

The book is intended for a wide circle of analytical chemists, chemistry teachers, post-graduates and students majoring in the field of analytical chemistry.